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TEXTILE RESEARCH JOURNAL

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Measurement of Crimp in Single Fibers[1]

Alexander Brown[2]

Carbide and Carbon Chemicals Company, South Charleston, West Virginia

Abstract

A technique is described for the measurement of the crimp content of fibers that is particularly applicable to fibers of high crimp content. The technique is adaptable to the measurement of the permanence to stretch of the crimp, and this permanence is correlated with the permanence to the stretches induced in fiber processing.

Introduction

Crimp in a fiber is a rather important feature for it holds fibers together in such a way that a mass of them has some cohesion and strength and at the same time it holds fibers apart so that the mass has bulk and loft. Thus crimp is of value in carrying staple fibers through the various stages of processing into yarns and in imparting bulk and loft to yarns and fabrics. Also, in the case of fabrics, it is quite likely that crimp imparts enough breathing space to the fibers that wrinkle resistance, wrinkle recovery, and abrasion resistance are also improved.

These important attributes of crimp in fibers require that a method of its measurement be available, and this need becomes more pressing when it is realized that in the man-made fibers the crimp content can be regulated over a rather wide range by a number of different crimping techniques.

There are several different ways to measure the crimp in single fibers. By crimp is meant the bends or waves in a fiber, and one method of measuring crimp content is to count the number of such bends per unit length of fiber [4]. This is a direct method and requires simple equipment. However, some fibers exhibit a wide variety of sizes and types of bends and sometimes also superposition of bends. In these cases, it is a problem to decide which bends will function as crimps, and thus should be counted, and which will be inoperative, and thus should be ignored. Moreover, the term unit length is itself definitive but the term unit length of fiber is not so easy to define. Length is most easily measured along a straight line; thus a fiber must be aligned somewhat for a crimp count. This requires force, and one soon finds that the length of the fiber varies with the magnitude of the aligning force and that some of the bends seem to disappear on alignment. These difficulties of crimp measurement may be removed by arbitrary decisions as to when a bend is a crimp and how long a fiber is. However, these decisions, to be useful, must be made with some correlative experience with the performance of the fiber in processing and in fabric behavior.

A second method of crimp measurement determines the crimp contraction, that is, how much the true length of the fiber is decreased by the incorporation of the bends. This involves the measurement of the

[1] Presented at the Fiber Society Meeting, Charlottesville, Virginia, May 6, 1954.

[2] Present address, Research Department, Bakelite Company, Bloomfield, New Jersey.

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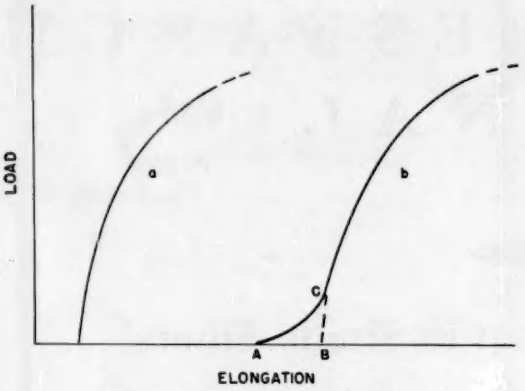

Fig. 1. Initial portion of load-elongation diagram of uncrimped fiber, *a*, and crimped fiber, *b*.

length of the fiber under a very small aligning force, sufficient to align the fiber but not to straighten out the small bends, and also under a larger force which is just sufficient to straighten out the bends. In this method, the decision of how large these loads should be has to be made, and again either an arbitrary decision or else correlation with fiber performance in processing and in fabrics is necessary.

Each of these methods can be made into useful measures of the crimp content of single fibers. As described, though, they afford no measure of a perhaps even more important aspect of fiber crimp—its permanence. Crimp is impressed on the synthetic fibers because their makers realize that it is necessary to carry the fibers through the various stages of processing into yarns and to impart some improved properties to the fabrics. The amount of crimp available to help the fibers through the advanced stages of processing depends on how much has survived the rigors of the previous stages. Thus a useful measure of single-fiber crimp should determine not only how much crimp is impressed on the fiber by the manufacturer or by nature, but also how much of this crimp is retained by the fiber after it has been loaded or stretched by amounts that are equivalent to those to be encountered by the fiber in textile processing. The latter is what is meant by crimp permanence.

Experimental

The technique for the measurement of crimp content and crimp permanence utilizes the load-elongation behavior of single fibers. The method depends on the fact that crimps in a fiber are bends and that the force required to unbend the crimps is less than that to stretch the fiber [1, 2]. Thus, when a crimped fiber is mounted in a relaxed state between the jaws of a single-fiber tester and the jaws are then caused to separate, the force on the fiber rises very slowly at first as the crimps start to open up, then more rapidly as they approach complete straightening out, and then very much more rapidly as the fiber is actually stretched. Figure 1*a* is the load-elongation diagram of a single fiber which contains no crimp and Figure 1*b*, that of the same fiber containing crimp. In the region bounded by the curve, the abscissa and the extrapolation corresponding to the true stretching load-elongation curve, *ABC*, the crimps in the fiber are being straightened out. This is thus called the uncrimping region. The length *AB* corresponds to the "contraction" of the crimp; the force *BC* corresponds to the uncrimping load or force. In the present technique, the area of the uncrimping region is measured, and this, of course, corresponds to the energy of uncrimping. That is, the measure of crimp content is a determination of how much work it takes to pull the crimp out of the fiber.

In the present work an Instron Tensile Tester was used throughout. The fiber samples were approximately 2 in. long. They were stretched at a rate of 10% per minute and the extension was magnified 100 times by running the chart at a correspondingly faster speed. Load sensitivities were chosen to yield optimum values of the uncrimping areas. Deniers were determined by using a vibroscope [3].

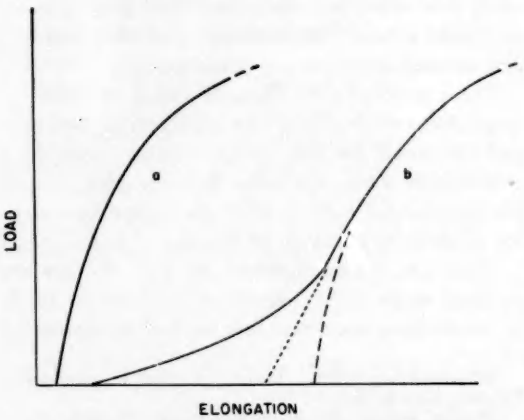

Fig. 2. Initial portion of load-elongation diagram of uncrimped fiber, *a*, and highly crimped fiber, *b*.

There are a number of advantages to this method of crimp measurement in single fibers. The arbitrary conditions, described as pertaining to the other methods, are chosen by the simple expedient of letting the fiber tester make the decisions both as to when is a crimp not a crimp and how long a fiber is. Actually, one is not really avoiding a responsibility in making such decisions, as the instrument in its integration of stress and strain is measuring perhaps the most important aspect of the crimp content—its ability to perform against externally applied forces. Also, since the fiber under test is mounted in an instrument normally used for loading and stretching fibers, it is obviously very easy to determine how permanent the crimp in the fiber is to different loads or extensions. Insofar as the processing of fibers into yarns embodies certain loading or stretching procedures, this information can then be used to determine how permanent the crimp in the fiber will be to textile processing.

One difficulty of the method shows up when the fiber contains a great deal of crimp. Figure 2 shows the load-extension curves of a fiber with no crimp (*a*); of the same fiber with a great deal of crimp in it (*b*). In the first curve the fiber is being stretched only, since there is no crimp present. In the second curve uncrimping and stretching occur, but the crimp content and the force necessary to pull it out are large comparable to forces which would impart a measurable stretch to the fiber. The result of this high crimp content and resulting high uncrimping force is that the uncrimping part of the curve merges with the stretching part of the curve rather high up on the latter, and, since the uncrimping part of the curve is concave upward and the stretching part is concave downward, the merging region approximates a straight line. This straight-line portion invites its use for extrapolation for the separation of the crimp and stretching portion of the curve, shown by the dotted line in *b*. This would be erroneous, however, for the true separation of these portions is really shown by the dashed line. Use of the dotted line extrapolation, which certainly appears a reasonable choice, would result in too low a value for the crimp content of the fiber, in too low a value for the stiffness, or modulus, of the fiber, in too high a value for crimp permanence, and in an apparent change of modulus with stretch.

Given a curve like that shown in Figure 2*b*, then, and realizing that an extrapolation of the "straight-line" portion of the curve will yield an erroneous measure of both crimp content and of fiber stiffness, how is one to determine the true crimp content and the true modulus of the fiber?

The problem is to determine what the load-extension curve would be if the fiber contained no crimp. Thus the direct approach is simply to remove the crimp from the fiber and then obtain the load-extension curve of the decrimped fiber. This crimp removal is readily achieved by stretching the fiber; the greater the imparted stretch, the greater the amount of crimp removed. The stretch that is impressed to remove or lower the crimp content also causes some changes in the load-extension curve subsequently measured for the decrimped fiber, however, and one must determine what these changes are. The changes that one might expect to follow a prestretching history would be in the initial modulus of the fiber and in its length (i.e., "permanent set").

For the determination of the crimp content of highly crimped Dynel, a number of measurements were first made on fibers which had not been crimped. These fibers were stretched various amounts and allowed to recover untensioned; then the change in modulus and length were noted as a function of extent of prestretch. The results of this examination are shown in Figures 3 and 4.

Figure 3 shows the values of the modulus of the fiber as a function of the amount of prestretch given the fiber. It can be seen that there is little change in modulus until the sample has been prestretched by

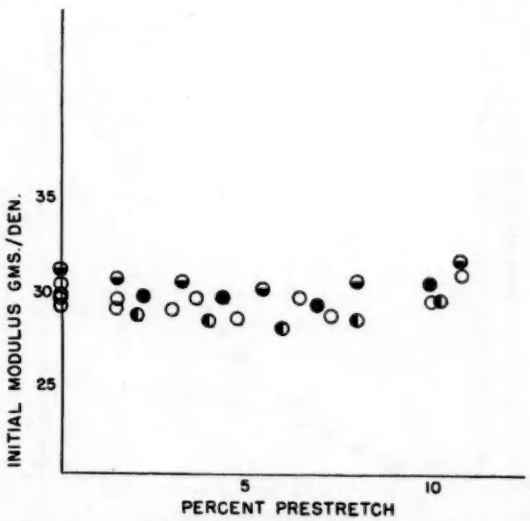

Fig. 3. Modulus of Dynel fibers as a function of the amount of previous stretch.

amounts greater than 7%. Figure 4 shows the "permanent set" resulting from these same stretches.

On the basis of the above results, a Dynel fiber, stretched 7% of its original length and then allowed to recover untensioned for 1 min, will show, on a subsequent measure of the load-elongation properties, the same initial modulus as the virgin fiber and the length of the fiber will be 2.8% greater than that of the virgin fiber. Also, from exploratory work on the permanence of crimp to stretching of the fiber, it was known that a stretch of 7% followed by a 1-min untensioned recovery would "permanently" remove a great deal of the crimp, an amount sufficient that little difficulty would be encountered in measuring it by the extrapolation technique.

Thus, to determine the crimp content of a highly crimped fiber, a load-extension diagram is obtained while stretching the fiber to 7% of its length. The fiber is then allowed to recover untensioned for 1 min, after which a second load-extension diagram is obtained. This second diagram is identical to the true-stretching portion of the first, except that it is displaced along the extension axis by an amount corresponding to 2.8% "permanent set" (it contains, however, a small residual crimp which is easily corrected for). All that is necessary is to slide the second load-extension curve to the left by the necessary amount and the first composite curve is resolved into its uncrimping and stretching portions. This is illustrated in Figure 5.

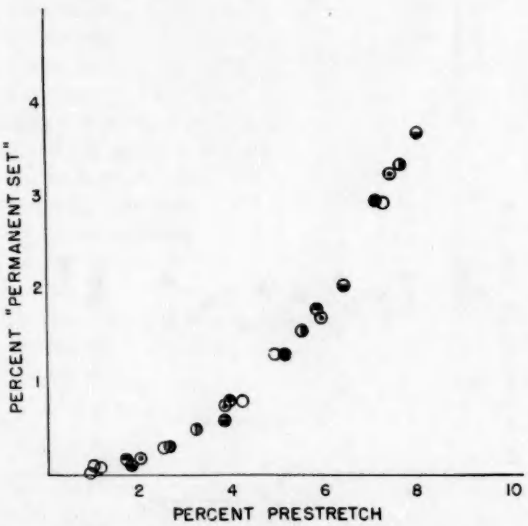

Fig. 4. Amount of "permanent set" induced by stretching Dynel.

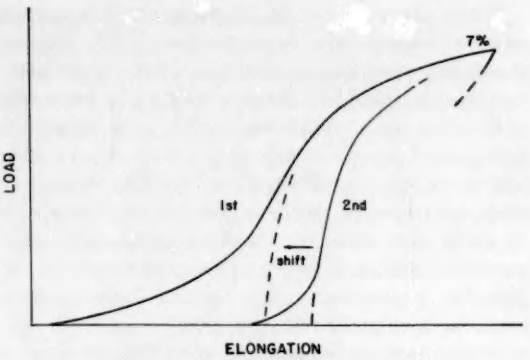

Fig. 5. Load-elongation diagrams illustrating the determination of the crimp content of highly crimped fibers. In this and the following figures the amount of shift has been exaggerated.

This technique is found to be necessary for crimp-content measurement on mechanically crimped fibers of a high crimp content, notably in Dynel, nylon, and Dacron.[3] It is not necessary with normal viscose or cotton, in which the crimp content is very low and easily measured by the simple extrapolation of the straight-line portion of the curves. The technique will not work for wool because one cannot remove enough of the crimp by stretching to get the true-stretch load-elongation curve. For this reason it is felt that all reported values of the crimp content and modulus of fine wools are too low.

There is a complication in the method which turns out to be minor but which should be explained. The operator will not know the true length of the fiber he is working with until the crimp has been pulled out. Therefore, he will not know how much he is stretching it nor, correspondingly, how much "permanent set" should be corrected for by the shift. It is thus necessary to assume that the fiber has been stretched, for example, 7%, during the first load-extension curve. The second curve is then shifted to the left by the amount of set known to be induced by a 7% stretch. This gives a "first" true length of the virgin fiber. From it the amount of stretch imparted in the first load-extension diagram can be calculated. This calculated stretch will be, in general, different from the assumed value, requiring a different shift and resulting in a different true length from that first obtained. This yields a different stretch from that first calculated, requiring another different shift, etc. The successive approximations rapidly converge, however, so that the process is not

[3] Du Pont polyester fiber.

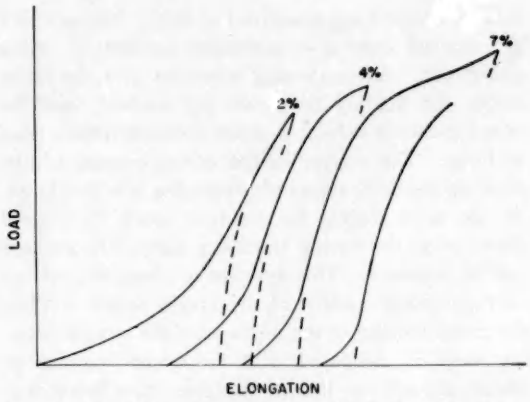

Fig. 6. Load-elongation diagrams illustrating the determination of the permanence of crimp in highly crimped fibers.

laborious. In fact, it can often be dispensed with if the operator can assume a stretch close enough to the actual or can stretch the fiber close enough to a predetermined level, using, in either case, the *stress* on the fiber as a guide.

The technique is readily applied to the measure of crimp permanence. The fiber is subjected to two intermediate stretches and recoveries before being subjected to the 7% stretch as in crimp content measurements. An example of the experimental record is given in Figure 6. A load-extension diagram is obtained while the virgin fiber is being stretched a small amount, e.g., 2%. The fiber is allowed to recover, untensioned, for 1 min; then a second load-extension diagram is obtained during a 4% stretch. After untensioned recovery, the fiber is stretched 7% and again, after recovery, stretched again far enough to establish the initial portion of the load-extension diagram of the decrimped fiber. The last curve is shifted to the left by the amounts corresponding to the "permanent set" induced by the different stretches. The uncrimping areas measure, in the first load-elongation curve, the crimp content of the virgin fiber. The crimp content that is still present after stretch and recovery from a 2% extension is given in the second curve, and that which is still present after stretch and recovery from 4% extension in the third curve, etc.

Similar measurements on a number of fibers would yield a curve like Figure 7. This shows the permanence of crimp to different amounts of stretch. Different crimp contents and different degrees of permanence, resulting from the use of different crimping techniques, would show different rates of fall-off with stretch (Figure 8).

While in principle the uncrimping area is used as the measure of crimp content, the actual calculation utilizes a simple approximation which has been shown to be valid for wool [2]. Comparison of the approximations with the planimetered areas shows that it is valid for Dynel also. Figure 9 shows the two parameters, Fo and X, that are used in the calculation. Fo is the ordinate of the curve at the true

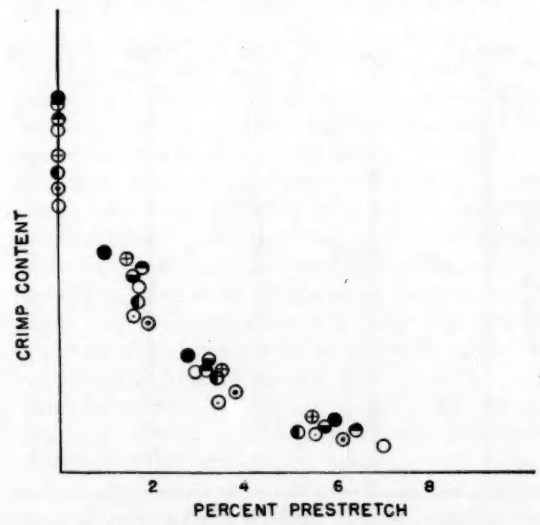

Fig. 7. Crimp permanence of different fibers from the same lot.

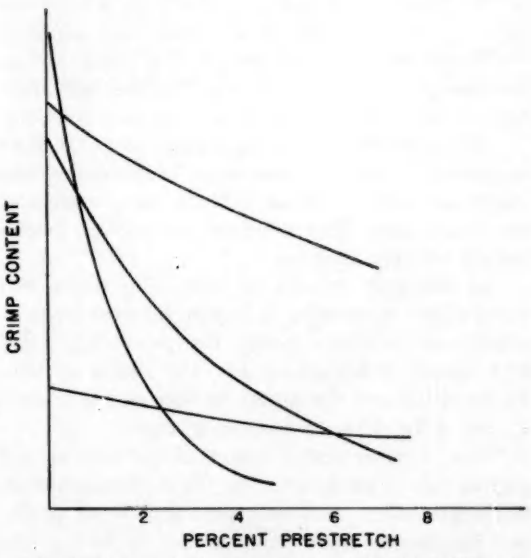

Fig. 8. Form of crimp permanence induced by different crimping techniques.

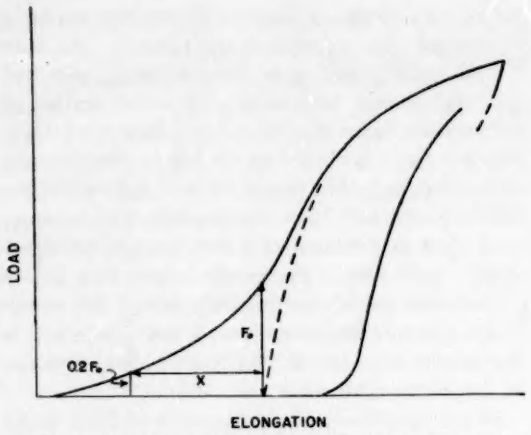

Fig. 9. Method of obtaining *Fo* and *X* from the load-extension diagram.

length point; X is the distance between this and the point at which the ordinate of the curve is 1/5 of *Fo*. The crimp content is calculated by

$$\text{Crimp content} = \frac{(Fo)(X)}{(d)(l)}$$

where d is the denier of the fiber and l is the true length.

Curves like those shown in Figure 8 are useful in the evaluation of the efficiencies of different crimping conditions impressed on a given fiber and in the comparison of the crimp in different types of fibers. They do not reveal, however, the permanence of the crimp to textile processing because one does not know the levels of stretch that occur during processing or the levels of stretch in the laboratory test that are equivalent to these processing stretches. To determine this, the crimp content of Dynel fiber was measured after various stages of processing into staple yarn and compared with the crimp content of the virgin fiber after different amounts of known stretch had been imparted.

The different systems of processing fibers into yarns might be expected to impart different levels of stretch to the fibers during the processing. The first system investigated was the cotton system. Figure 10 shows the crimp content of fibers after certain of the different processing stages.

There is considerable scatter in the results, and part of this is inherent in the crimp distribution in the virgin fiber. However, part is a result of the fact that there is not a complete fiber by fiber working during processing, and many fibers float through the early stages without being subjected to forces sufficient to pull any crimp out of them. Those which get worked have a considerable amount of crimp pulled out. As processing advances into the latter stages the floating fibers do get worked, and the crimp contents exhibit a more constant value, fiber to fiber. The scatter in the crimp content of the fibers in the early stages of processing is rather large. In the later stages, for example after the second drawing on the roving frames, a significant average can be obtained. This average is about half of the average crimp content of the virgin staple. When the crimp content of the fibers after the second drawing stage is compared with the crimp contents of fibers subjected to known stretches, it is found that the crimp content of the processed fiber is the same as that of virgin fibers that have been stretched 3% of their length and then allowed to recover untensioned.

The scatter in the crimp content of fibers extracted from the yarn stage of processing is greater than in fibers from the roving stage, probably due to the inclusion of a certain amount of fiber twist in the crimp-content measurement. For this reason the yarn stage is excluded from the correlations with laboratory tests in this and other processing systems to be described.

The stretches impressed on the fibers during processing on the cotton system are not, however, of the order of 3%. The processing stretches are imparted much more rapidly than the few seconds used in the laboratory test. Also, the fibers are allowed

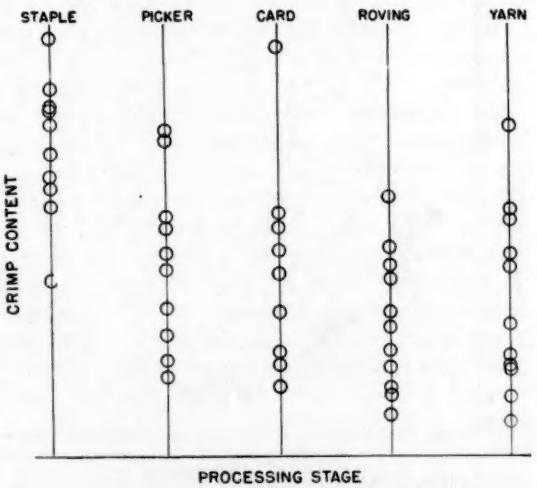

Fig. 10. Crimp content of Dynel fibers at different stages in cotton-system processing.

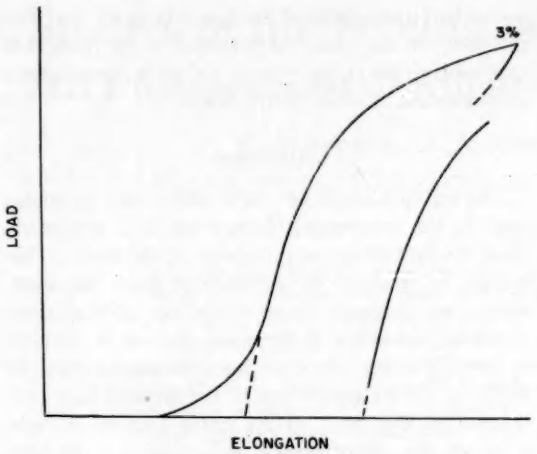

Fig. 11. Load-elongation diagrams illustrating determination of crimp permanence to cotton-system processing. Low crimp fiber.

a much longer time to recover from stretch in processing than the 1 min allowed in the laboratory test. Each of these differences in time schedule would indicate that the actual stretches suffered by the Dynel fibers in processing are greater than 3%. However, operating at the convenient time schedule of the laboratory test, the fiber will lose as much crimp on being stretched 3% as it will on being processed through the roving stage in the cotton system.

The laboratory method of determining the crimp content and crimp permanence of fibers to be processed on the cotton system would then be as follows. The load-extension curve of the fiber would be obtained while the fiber was being stretched 3% of its length. A period of 1 min would then be allowed for the untensioned recovery of the fiber. A second load-extension curve would then be obtained. If the crimp content of the fiber is small so that separation of the uncrimping and stretching portion can readily be made, this second curve need be obtained only far enough to obtain the straight-line portion of the curve. If the crimp content is large, this second load-extension curve should be carried to about 7% stretch (for Dynel). In the latter case, a 1-min untensioned recovery period would again be allowed, after which a third load-extension curve carried beyond the straight-line portion would be obtained, this third curve being used in the shifting process previously described. The second load-extension curve yields the crimp content that is permanent to 3% stretch and thus to cotton system processing. The types of load-extension diagrams that might be obtained are shown in Figure 11 for a low crimp-content fiber and in Figure 12 for a high crimp-content fiber.

It might well be emphasized at this point that crimp content of a fiber is the most sensitive measure of low-load mechanical history of the fiber. This is illustrated by the results obtained in the investigation of crimp content as a function of processing on the cotton system. The change in crimp content amounted to about 50%, corresponding to an exposure to a 3% stretch followed by untensioned recovery. Such a stretch and recovery does not measurably alter the stiffness or modulus of the fiber, nor would it alter the "yield" region properties of the fiber. Any changes in the tenacity or elongation of the fiber would be within the experimental errors of these measurements. The 3% true stretch of the fiber would be about 90% recovered during the time allowed for recovery so that the fiber would be about 0.3% longer as a result of this stretching history. This change in length would readily be measured if the history were applied while the fiber were mounted in a single fiber tester but certainly could not be used to determine the history of the fibers in one mass compared to that of those in another. Crimp-content measurements thus offer a potentially useful technique for the investigation of such low-load histories.

The crimp permanence and the associated laboratory test methods have also been investigated for the Pacific Converter system and, to a limited degree, for the worsted system. Figure 13 shows the crimp

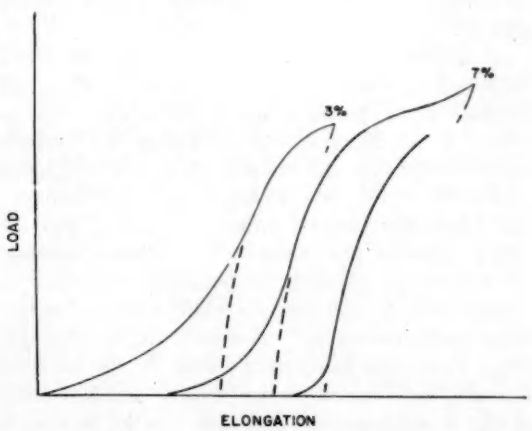

Fig. 12. Load-elongation diagram illustrating determination of crimp permanence to cotton-system processing. Highly crimped Dynel.

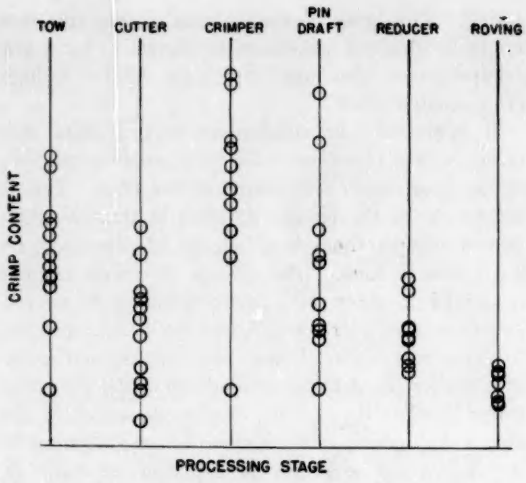

Fig. 13. Crimp content of Dynel fibers at different stages in Pacific Converter system processing.

content of fibers as a function of processing in the Pacific Converter system.

As might be expected, this method of yarn manufacture is considerably rougher on the fibers than the cotton system. It is found that about 75% of the crimp is lost through the roving stage. The measure of crimp permanence as a function of stretch in the same fibers reveals that the average stretch imparted to fibers through the roving stage is equivalent to a 5% laboratory stretch.

The worsted results are limited. However, a figure of 5% (the same as the Pacific Converter system) is probably very close to the correct value for the laboratory stretch equivalent to the average amount of stretch imparted to fibers processed on the worsted system.

It should be realized that the amount of stretch imparted to fibers in processing will depend on the settings of the machines and on the frictional properties of the fibers arising from both the intrinsic nature of the fiber and of the finish or lubricant added to it. Therefore, the correlations presented between the laboratory tests of crimp permanence and the crimp losses in processing on the different systems, should, strictly speaking, be described as applying to Dynel under certain machine settings and using certain finish formulations. However, the machine settings and finish formulations used in the different systems were chosen on the basis of practical processing considerations, and this should bestow a somewhat more general interpretation on the correlation. In any case, the principle of the method is applicable to the crimp content and crimp permanence measurement of other textile fibers.

Summary

The crimp content of single fibers may be measured by the uncrimping energy which is obtainable from the load-elongation diagram of the fiber. This energy is obtained by subtracting from the load-elongation diagram the contribution arising from stretching the fiber. If the crimp content of the fiber is low (viscose, cotton), this subtraction may be made by the extrapolation of the straight-line portion of the diagram. If the crimp content is high, however, this extrapolation is erroneous. In such cases, one must find the contribution from stretching by supplementary measurements which involve pulling the crimp out of the fiber, determining the load-elongation properties of the decrimped fiber, and correcting them for the history acquired during the pulling out of the crimp. This method works for the synthetics but not for wool, where crimp cannot be pulled out. A useful laboratory measure of the permanence of crimp in fibers can be made by noting how much remains in the fiber after stretching it 3% if the fiber is to be processed on the cotton system. If the Pacific Converter or worsted system is to be used to process the fiber, then a 5% stretch should be used in the measurements.

The crimp content of the fibers is probably the most sensitive indicator of histories involving low loads or extensions and thus might prove a useful tool for the study of textile processing itself.

Acknowledgment

It is a pleasure to acknowledge the assistance of Mr. Richard C. Gross, who obtained most of the experimental results presented here.

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Studies of the Dyeing of Nylon with Acid Dyes

Part I: Measurement of Affinity and the Mechanism of Dyeing

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Abstract

The dyeing of nylon with acid dyes has been investigated in greater detail than hitherto and the mechanism postulated by earlier workers has been confirmed, with minor reservations. The affinities for nylon of 12 acid dyes have been determined by desorption with inorganic anions and a more generally applicable equation has been evolved for the relationship between desorption data and affinity. This equation is based upon statistical thermodynamic consideration of the dye-fiber system, and the validity of its application to dye and inorganic anions of any basicity is confirmed by the experimental data. The results obtained have enabled some conclusions to be reached regarding the effect on affinity of structural variations within a related series of dyes. A comparison of the data for nylon with the well-established values for wool has shown a satisfactory measure of agreement.

Introduction

As a result of previous investigations [3, 15], the following mechanism is now accepted as accounting for the uptake of acid dyes by nylon. On immersion of the fiber in a dyebath containing acid and dye, hydrogen ions are absorbed onto carboxyl groups and the more slowly diffusing dye ion is then able to attach itself to the positively charged amino groups. This picture is similar to that for the adsorption of these dyes by wool and may be represented schematically as

$$NH_3^+NyCOO^- + H^+ + D^- \rightarrow D^-NH_3^+NyCOOH$$

where Ny is the nylon chain separating the end amino and carboxyl groups and D^- is a dye anion (monobasic for simplicity).

The titration curve of nylon is similar to that of wool, being sigmoid in shape and reaching a fairly well-defined maximum corresponding to saturation of the amino groups. The titration curves obtained by dyeing nylon from baths of varying *p*H containing large concentrations of dye have been described in detail elsewhere [15, 17]. They are not as simple as would be suggested by the above mechanism and show, apart from the sigmoid portion in the region of *p*H 5–8, an almost horizontal plateau which corresponds to the quantity of amino groups in the fiber. However, when the *p*H reaches 2.5 there is a rapid increase in uptake with further lowering of *p*H, and this increase apparently does not reach a maximum. (Typical curves are reproduced in Figure 1.) This has been referred to as "overdyeing" [12, 15].

In normal dyeing, the *p*H is greater than 2.5, and hence dyeing is in the main associated with the amino groups in the fiber. The lack of buildup of dyes on nylon is due to the small number of terminal amino groups available (ca. 40 meq/kg of fiber), leading to low saturation values and excessive competition for the limited number of dyeing sites when mixtures of dyes are applied. The heights of the plateaus correspond approximately to the number of sulfonic acid groups in the dye molecule. This simple stoichiometric relationship does not explain all the dyeing behavior for in the *p*H isotherms determined by Peters [15] (Figure 1) residual differences in the heights of the plateaus of the different dyes were apparent. Some of the saturation values (plotted in terms of equivalents) were lower than the amine end-group content of the fiber, the extreme behavior of the dyes studied being shown by Solway Blue B with a saturation value of 30 and Naphthalene Red J with a value of 45 meq/kg. Similar deviations from stoichiometry have been noted by American workers [11, 17], who attributed the lower saturation values of the disulfonated dyes to the difficulties of fitting the dye molecule onto the fiber sites. Similarly, Lemin [9], in studies of the uptake of free dye acids of Naphthalene Red EA and Solway Blue B in the absence of foreign electrolytes, found by extrapolation of a reciprocal plot of the titration curves

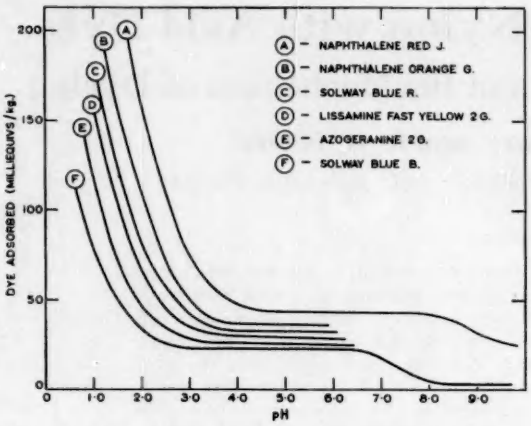


Fig. 1. Variation of equilibrium dye uptake with change in *p*H (from an earlier work [13]).

that the former dye had a saturation value of 37 and the latter 28 meq/kg of fiber.

From what has been said, it will be apparent that the simple mechanism previously postulated for the dyeing process involving amino groups does not take account of all the influences governing dye adsorption and it seems likely, as suggested by McGrew and Schneider [11], that one of the sources of breakdown is the difficulty of disposition of the dye anion within the fiber. When it is remembered that dye molecules are relatively bulky entities which must be accommodated in close proximity to the regions of the fiber in which the amino groups are located, it is rather surprising that the simple stoichiometric relation is observed to the extent which occurs in practice.

The adsorption of dye is further complicated by the fact that overdyeing occurs without degradation; i.e., the fiber can absorb dye in excess of the amount corresponding to its amino groups [12]. The *p*H at which this occurs varies with the dye (Figure 1) and is dependent upon the nature and size of the dye molecule and the degree of sulfonation, large planar molecules tending to increase the overdyeing (e.g., Naphthalene Red J) and the additional sulfonic acid groups tending to reduce it (e.g., Solway Blue B). Thus the titration curves which have been determined using a dyebath containing an arbitrarily high concentration of dye, as has been carried out by earlier workers, are not sufficient for a quantitative specification of the physicochemical nature of the equilibrium. For this reason some further studies on the overdyeing properties of a number of acid dyes have been made with a view to demonstrating the differences in the extent of overdyeing shown by the various dyes.

Having established a likely dyeing mechanism, it is then of considerable interest to study the energetics of the dyeing process and to obtain quantitative physicochemical data relating to the dye/fiber interaction. When equilibrium studies are made, the relevant quantity is the partial molar free energy change which occurs when 1 M of dye is transferred from dyebath to fiber under standard conditions. This quantity gives a measure of the tendency of the dye to be absorbed, and its use in dyeing investigations has led to a more complete understanding of the dyeing process than would have been possible using the concepts of practical dyeing.

To derive an expression for the free-energy change from dye-absorption data, however, is not completely straightforward since it is necessary to represent satisfactorily the activities of a dye in the aqueous and fiber phases. For nylon, a fiber whose dyeing is connected intimately with the number of amino groups, the assumptions concerning the state of adsorption are similar to those made in wool dyeing theory. These are that the dye in adsorbed as a monolayer onto a set of localized sites in the fiber (i.e., amino groups). This method of representing dye adsorption was first used by Gilbert and Rideal [7] and has been more recently applied to nylon by McGrew and Schneider.

The present paper is concerned also with the choice of a suitable adsorption model and with affinity studies of 12 acid dyes. It is divided into three sections:

1. Experiments to assess the extent to which stoichiometric uptake of dye occurs.
2. Theoretical derivation of a thermodynamic formula suitable for affinity measurements.
3. Affinity determinations based on this formula.

1. *Investigations of Stoichiometry*

a. *Materials.* The nylon used throughout the work described in this paper was 15 den microdull monofil which had an amino-group analysis of 35 meq/kg. The end-group analyses were determined on several samples of the batch by dissolution in phenol/methanol and titration with $N/20$ hydrochloric acid, using Thymol Blue as the indicator. The results varied by not more than 5%.

For the dyeings, commercial samples of the dyes were used. The dye content of these was deter-

mined by comparison with electrolyte-free material obtained by precipitation of the commercial dye from solution by addition of sodium acetate three times followed by two or three crystallizations from water or alcohol/water mixtures until solutions of the material gave constant optical densities.

All other materials were of A.R. quality.

b. *Method of dyeing.* Preliminary dyeings were carried out in which the fiber (0.13–0.14 g) was dyed for 24 hr at 75°C, using a dyebath of 50 cc containing an excess of dye (0.004 m/l where possible) and varying amounts of formic acid in order to obtain *p*H values ranging from 4.5 down to 2.6. (With one or two dyes it was necessary to use more dilute solutions owing to their low solubilities; in these cases a larger volume of liquor was used to avoid exhaustion of the dyebath.) The time allowed was adequate for the fiber to reach equilibrium at this temperature, and the dyebath exhaustion was less than 2%. Under these conditions of high dye concentration the fiber was able to adsorb enough dye to reach approximate "saturation."

At the end of the dyeing period the fiber was removed from the bath, washed free of extraneous dye solution, dried in an oven for 2 hr at 70°C, cooled in a desiccator for 1 hr, and weighed. The material was dissolved in *o*-chlorphenol and the amount of dye determined optically by means of a Cary Recording Spectrophotometer.

In order to minimize any error which might otherwise have arisen from modification of the absorption spectra of the dyes by the nylon present in solution, the optical-density measurements were compared with similar solutions made from fiber dyed to a known depth of shade from a finite dyebath. In these estimations, a small correction was made for the optical density arising from the small amount of titanium dioxide present. Some of these results are plotted in Figure 2 as milliequivalents of dye adsorbed against *p*H of the dyebath.

It can be seen that a significant variation of behavior exists between the dyes, both in the milliequivalents of dye on the fiber at a given *p*H and the variation of this quantity with *p*H. The behavior of the dyes which have saturation values below the amino-group content of the fiber (taken in this case as 35 meq/kg) can be explained in terms of the incomplete accessibility of all the amino groups to the dye anion, but even in these cases there is evidence of a gradual increase of dye uptake with decrease of *p*H. The dyes with saturation values above 35 meq/kg show a more marked *p*H sensitivity.

Because of the differences of behavior shown under these conditions, further measurements were carried out to investigate the deviation of dye uptake from the stoichiometric quantity corresponding to the amino-group content of the fiber. The "*p*H" isotherms show that considerable differences exist between the dyes. The gradual increase of dye adsorption is probably due to adsorption of undissociated dye onto amide groups or hydrophobic portions of the nylon crystallites. If this is so, dye uptake will depend on two variables, namely, the *p*H and concentration of dye, in contrast to the dye adsorbed on amine end groups, which will be virtually independent of these variables once saturation has been achieved. Thus, determination of the amount of dye associated with the amino groups cannot readily be determined from experiments of this type. Isotherms in which the *p*H was kept constant and the concentration of dyestuff varied were therefore determined. The fiber was dyed under conditions similar to those described above, with the modifications that a phosphate buffer was employed to ensure that a constant *p*H of 3.2 was maintained and the dye concentrations were varied from 0.0004 to 0.0032 M. While the use of a buffer is the most convenient way of ensuring a constancy of *p*H throughout the dyeing, it does have the disadvantage of reducing the amine-group adsorption. This reduction is, however, very small since there was very little difference (<5%) between the dye uptake from formic acid and from buffer. The results for some of the dyes

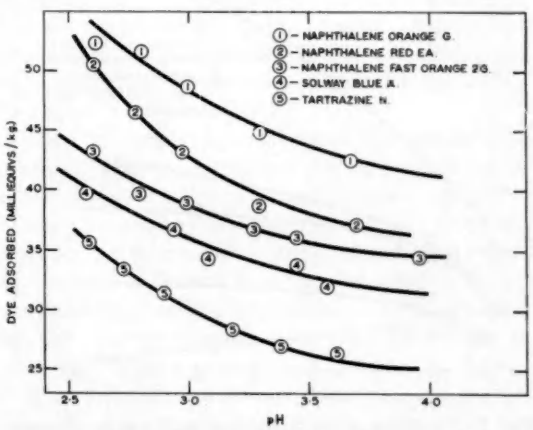


Fig. 2. Variation of equilibrium dye uptake with change in *p*H. Temperature 75°C.

are shown graphically in Figure 3, where the quantity of dye on the fiber is plotted against the concentration in solution at equilibrium. For the low dye concentrations, the amount of dye on the fiber increased rapidly to reach a maximum with some dyes (e.g., Naphthalene Fast Orange 2G) when further increases in dye concentration did not appreciably alter the amount of dye on the fiber or, for dyes with neutral dyeing properties, continued to increase approximately linearly but at a considerably smaller rate.

c. *Discussion.* From the adsorption isotherms at varying *p*H (Figure 2), the individual behavior of the dyes and the different saturation values can be seen. The isotherms have a characteristic shape and demonstrate that, in addition to overdyeing at low *p*H values, the plateaus are for most dyes not horizontal, but, rather, small increases in dye uptake occur as the *p*H is lowered from, say, 5 to 3. There is, of course, no reason why the onset of overdyeing should occur entirely at low *p*H's and the fact that the plateaus are inclined indicates that overdyeing occurs to a lesser or greater extent at all *p*H values once saturation of the amino groups has been achieved. This is in accord with the suggestion that overdyeing arises from adsorption of the undissociated dye acid onto amide groups in the fiber. The magnitude of the effect will depend on the affinity of the dye and the concentration of undissociated dye acid in the bath. The latter will in turn depend on the *p*H and concentration of dye.

Thus it was not possible to determine the extent to which the dyes saturated amino groups from the isotherms where the *p*H was varied, and this information had to be obtained from those in which the dye concentration was varied (Figure 3). These curves are characterized by high adsorption of dye at low concentrations followed by a flat or slowly increasing portion, in accord with the idea that the first quantity of dye is absorbed onto amino groups and any further increase in dye uptake may be regarded as "overdyeing." The extent of the latter is determined by the slope of the subsequent part of the graph. Most of the dyes showed linear increases or horizontal straight lines, with the exception of one or two of the monosulfonated dyes such as Naphthalene Orange I (Figure 3), where the curve deviated from linearity at the higher concentrations. It was therefore possible to extrapolate these graphs to zero concentration to obtain the saturation value with respect to amino groups. Such an extrapolation to some extent eliminated the effect of electrolytes present in the commercial dyes employed in this work. The effect of the electrolyte was to reduce the solubility of the dye in those baths containing high concentrations of dye, thereby reducing the amount of dye adsorbed. This point is shown in the isotherm for Tartrazine N, although it is quite clear that this adsorption is independent of dyebath concentration. Twelve dyes have been treated in this way, and the results are summarized in Table I by the intercept at zero dye concentration and the slope of the isotherm.

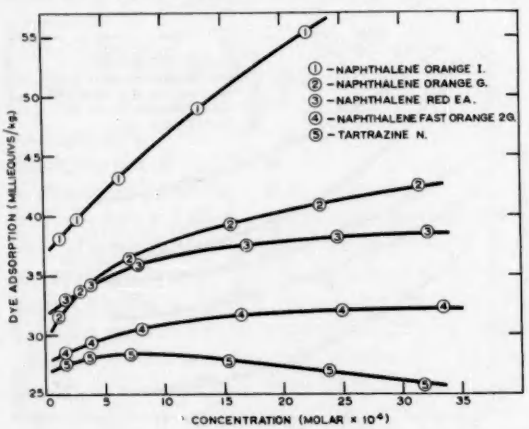


Fig. 3. Variation of equilibrium dye uptake at *p*H 3.0 with change in dyebath concentration.

The values given for the intercepts are near the amine titer of 35 meq/kg of fiber and substantiate the argument that the dye which is first adsorbed is taken up by amino groups. Those values which are substantially below the amine titer are for di- or tribasic dyes of low affinity; and this undoubtedly arises from the difficulties in accommodation by the fiber of molecules containing more than one sulfonic acid group. In the last column are quoted the affinities of the dyes (see also subsequent section). A comparison of the basicity and affinities of the dyes with the overdyeing as determined by the magnitude of the slope shows that the monosulfonated dyes overdye to larger extents than polysulfonated ones, as also do those dyes with high affinities, such as Naphthalene Red J and Naphthalene Red EA. The observed properties of the monosulfonated dyes are to be expected since they will more readily form undissociated dye molecules than the polysulfonates (assuming that the dissociation of the sulfonic acid

TABLE I

Dye	Color Index Number	Number of Acid Groups	Intercept (meq/kg)	Slope (eq/kg/M)	Affinity (kg-cal/M)
Naphthalene Red J	176	1	35	55.0	−7.66
Naphthalene Red EA	182	2	35	1.3	−6.52
Naphthalene Orange I	150	1	37	10.0	−6.17
Naphthalene Orange RO	161	1	36	2.5	−6.03
Naphthalene Scarlet 4R	185	3	37	0.4	−5.88
Naphthalene Orange G	151	1	35	2.5	−5.82
Lissamine Fast Yellow 2G	639	2	34	0.3	−5.31
Azogeranine 2G	31	2	34	0.0	−5.11
Solway Blue BN	1054	2	30	0.0	−5.05
Naphthalene Fast Orange 2G	27	2	30	0.7	−5.01
Tartrazine N	640	3*	28	0.0	−5.01
Solway Blue A	—	2	30	0.0	−4.67

* Tartrazine N is the sodium salt of a disulfonated carboxylic acid which, under acid dyeing conditions, behaves as a triacidic dye.

groups is of the same order in all the dyes). To confirm these overdyeing properties some nylon was acetylated so that its amine end group titer was reduced to 2.9 meq/kg and dyed at *p*H 3.2, using a dyebath containing dye at a concentration of 0.004 M. The amount of dye taken up is very much reduced and may be compared with the slopes (Table II). It is seen that a large value of the slope means a large quantity of dye absorbed. It is likely that this is a more sensitive test for overdyeing than the isotherms since the measurements are not complicated by the presence of dye absorbed on the amino groups.

Thus, the following picture of dyeing of this fiber with acid dyes emerges. At low dye concentrations, dye is adsorbed on amino groups. The total quantity of dye capable of being adsorbed onto these groups is approximately equal to the number of amine groups in the fiber, as suggested by earlier workers. The present work, however, indicates that for polysulfonated dyes of low affinity this saturation value may be reduced because of the difficulties of accommodation of the sulfonic acid groups in the fiber. Such a reduction is not evident with dyes of high affinity. As the concentration of dye in the bath or the acidity of the latter is increased, the fiber can adsorb excess dye as the undissociated dye acid. The extent of the overdyeing is dependent upon the degree of sulfonation of the dye molecule and on the affinity of the dye.

TABLE II

Dye	Number of Acid Groups	Slope (eq/kg/M) [ex Table I]	Uptake by Acetylated Nylon (meq/kg)
Naphthalene Red J	1	55.0	46.6
Naphthalene Orange I	1	10.0	41.1
Naphthalene Orange RO	1	2.5	23.0
Naphthalene Orange G	1	2.5	17.2
Naphthalene Red EA	2	1.3	11.0
Naphthalene Fast Orange 2G	2	0.7	5.2
Lissamine Fast Yellow 2G	2	0.3	5.5
Azogeranine 2G	2	0	8.3
Solway Blue A	2	0	5.4
Naphthalene Scarlet 4R	3	0.4	3.0
Tartrazine N	3	0	2.5

2. *Derivation of a Thermodynamic Formula*

From the foregoing discussion it may be assumed that the first quantities of dye which are taken up by nylon from a dyebath are associated in some way with amino groups. Since in dyeing practice the concentrations of dye which are used are considerably lower than those employed in the previous section, attention may be confined, for this purpose, to amino-group dyeing. This makes the problem similar to that encountered in the dyeing of wool. The adsorption of ions (e.g., hydrochloric and dye acids) has been treated by Gilbert and Rideal [7] and by L. Peters and Speakman [14].

These authors have used models to represent the system. The former treated the fiber as a lattice containing sites and applied the statistical mechanics relating to localized monolayers; the latter regarded the fiber as a homogeneous phase containing carboxyl groups with a Donnan membrane equilibrium of the ions existing between this phase and the external solution. (This is analogous to a gelatin solution in a semipermeable membrane.)

Both these approaches are able to account for the adsorption of simple acids but a controversy has raged as to which is to be preferred. Work by

Olofsson [13] had indicated that the fixed-site approach gives a better fit to the experimental facts and this is particularly so when dye acids are considered, since both ions must be attached to the wool. It was therefore adopted initially in this work.

The affinity or free energy change, $\Delta\mu^0_{HD}$ (referred to a suitable standard state), which occurs when one mole of a monobasic dye acid of formula HD is adsorbed by wool is defined by a formula of the type

$$-\Delta\mu^0_{HD} = RT \log a_f - RT \log a_s \qquad (1)$$

where a_f and a_s are the activities of the dye on the fiber and in the external solution respectively. Since no data are available on the activities of dyestuff solutions, the term a_s is replaced by the ionic product, i.e., $[H] \times [D]$, where $[H]$ and $[D]$ are the concentrations of the hydrogen and dye ions in solution. The expression for the activity on the fiber may be deduced on the basis of the model of fixed sites and turns out to be of the form

$$\frac{[H_F]}{S - [H_F]} \times \frac{[D_F]}{S - [D_F]}$$

where $[H_F]$ and $[D_F]$ refer to the concentrations of hydrogen and dye ions on the fiber and S is the saturation value. This expression may be substituted into equation 1 to give the following results:

$$-\Delta\mu^0_{HD} = RT \log \left(\frac{\theta_H}{1 - \theta_H}\right)\left(\frac{\theta_D}{1 - \theta_D}\right) - RT \log [H][D] \qquad (2)$$

where θ_H and θ_D are equal to $[H_F]/S$ and $[D_F]/S$ and are the fractions of sites occupied by the hydrogen and dye ions. Equation 2 enables the affinity to be calculated from an experiment in which fiber is dyed to equilibrium from a bath containing known concentrations of hydrogen and dye ions. In practice, it is often easier to use a competition technique in which the dyed fiber is put into a bath containing an acid together with the sodium salt of this acid. The presence of the acid enables the amount of hydrogen ion on the fiber to remain constant while competition for the positively charged sites takes place between the acid and dye anions. The relative amounts of the ions on the fiber and in solution at equilibrium enable the difference in affinity between the ions to be calculated as follows. The expression for the activity of the dye acid given in equation 2 involves the ratio of occupied sites to those unoccupied. Hence, to allow for the presence of a second ion, this equation must be modified to

$$-\Delta\mu^0_{HD} = RT \log \left(\frac{\theta_H}{1 - \theta_H}\right)\left(\frac{\theta_D}{1 - \theta_D - \theta_A}\right) - RT \log [H][D] \qquad (3)$$

A similar expression exists for the second acid, HA, and to obtain the affinity difference this may be subtracted from equation 3 to give

$$-(\Delta\mu^0_{HD} - \Delta\mu^0_{HA}) = RT \log \frac{\theta_D}{\theta_A} - RT \log [D]/[A] \qquad (4)$$

So far, attention has been confined to the adsorption of monobasic ions. In this case the physical model is clear since it is possible to occupy each $-NH_3^+$ site with an anion of either kind and each COO^- site with a hydrogen ion. All sites are assumed to be independent, and those of the same kind, whether amino or carboxyl groups, are assumed to be of equal energy. By such simple assumptions it has been found possible to account for the adsorption of acids and dyes by wool [10] and to obtain a substantially constant value of

$$-\Delta\mu^0_{HD} \quad \text{or} \quad -(\Delta\mu^0_{HD} - \Delta\mu^0_{HA})$$

The essential simplicity of the treatment arises from the assumption of identity of dyeing sites for the two types of anions present. This is undoubtedly valid for monobasic dyes. For polybasic dyes the picture cannot be made as simple as this. The most salient experimental fact for a system of this type is that the dyes are absorbed stoichiometrically, and this in particular applies to acid dyes on nylon. This point was confirmed on the latter fiber by dyeing mixtures of two dyes of the same and different basicities so that the fiber was saturated with dye [1]. In these experiments the ratio of the concentration to dyes was varied from 100% of one to 100% of the other; the total quantity of dye in terms of equivalents taken up remained constant within the limits of experimental error.

It is, however, difficult to visualize how a polybasic dye can physically saturate fixed sites (the amino groups). Because of this Gilbert and Rideal assumed the dye anions to be attached to one site, the stoichiometric relationship arising from the necessity of over-all electrical neutrality.

This led them to postulate an equation for a_f for a dye of basicity of

$$\left(\frac{\theta_H}{1-\theta_H}\right)^z\left(\frac{\theta_D/z}{1-\theta_D/z}\right) \qquad (5)$$

where θ_D is Equivalents of dye/Saturation value of fiber.

However, this formula is based on the assumption that each amino group is equally available to a dye molecule; this is obviously a simplification in that if one dye molecule is attached to an amino group, adjacent amino groups are equally available. This does not seem likely. Further it leads to a formula which lacks symmetry in that the part of the expression which is derived for the dye anion, i.e.

$$\theta_{D/z}/(1-\theta_{D/z})$$

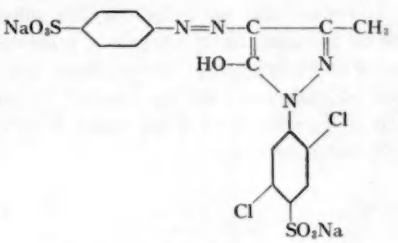
(and the expressions for the two ions are derived independently), has a maximum value of $1/(z-1)$, and hence a_f cannot take on all values from 0 to ∞, as would be anticipated in an idealized picture of this kind. It seems worthwhile, therefore, to consider what is the most reasonable model to assume.

The fundamental basis of these formulas is statistical mechanical in nature. In the simple case of monovalent ions the fiber is replaced by a lattice of fixed sites which are of the same energy with no interaction between them. On such a basis the partition function for the system may be constructed very simply. In the terminology of Fowler and Guggenheim [5], this is given by $g(n)[a(T)]^n$ for n molecules. In this equation $a(T)$ is the partition function for the internal degrees of freedom of the adsorbed molecule and $a(n)$ the combinatory formula denoting the number of distinguishable ways the n molecules can be arranged in the total of N sites. In this instance it becomes

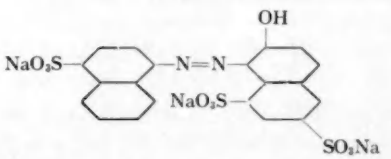
$$\frac{N!}{n!(N-n)!}$$

Unfortunately, when a polybasic dye is considered, the computation of the combinatory formula is coupled to the detailed nature of the lattice. A case which at first sight may be taken as analogous may be mentioned. In the discussion of athermal mixtures of liquids by Guggenheim [8], the quasilattice of Fowler is used. In this the liquid is regarded as a lattice of coordination number z; i.e., each site in the lattice has z neighbors. The problem then is to calculate the number of distinguishable ways in which molecules occupying 1 site (monomer) may be introduced into the lattice simultaneously with different molecules which are occupying physically, say, r sites (r-mer). The combinatory formulas for such a system are complex and involve considerations such as the probability of whether neighboring sites will be filled with a r-mer or a monomer. The problem is even more formidable when applied to mixtures of, say, s-mers and r-mers (where $s \neq r$ and s and $r > 1$).

The situation with fibers such as nylon is not the same as the classical kind just discussed. It seems unlikely that a lattice of fixed sites should be assumed since acid dyes as a class are composed of a diverse collection of compounds when the positions of, and distances between, the various sulfonic acid groups are considered. This is shown in the formulas for Lissamine Yellow 2G and Naphthalene Scarlet 4R, to quote two examples.



Lissamine Fast Yellow 2G (C.I. No. 639)



Naphthalene Scarlet 4R (C.I. No. 185)

Thus to replace the amino groups in the fiber by a regular geometric lattice onto which are fitted idealized regularly shaped dye molecules is to assign a degree of precision and regularity to the system far in excess of that occurring in practice. This type of divergence between a practical system and its representative theoretical model may sometimes be justifiable, but in the present case the assumption of a geometrically regular ideal lattice has little to recommend it.

For instance, difficulties arise in disposing polybasic molecules on the lattice in the vicinity of an edge of the latter. Further, if attempts are made to introduce any dibasic and tribasic molecules, then

many of the configurations result in deviations from stoichiometric uptake of as much as 40%, in contradiction to the observed stoichiometric behavior of mixtures of molecules having these degrees of sulfonation.

In view of this incompatibility between the rigid statistical mechanical approach and the observed facts of dye uptake by nylon, the treatment given subsequently is a simplified one in which the guiding principle has been that consistency with stoichiometry must be maintained.

Thus the model used for the accommodation of a z-basic ion allows the amino groups in the fiber to be divided up into N/z groups which are energetically identical. The value of $g(n)$ for the introduction of n molecules then becomes

$$\frac{N/z!}{n!(N/z-n)!}$$

However, there is nothing in the argument so far which indicates that, once the dye has taken up a position on the fiber chain, there is a preferred position for it to be oriented. Hence, there are z ways in which the molecule could be oriented; by assuming therefore a degeneracy of z this value of $g(n)$ must be multiplied by z^n to give

$$\frac{z^n N/z!}{n!(N/z-n)!} \tag{6}$$

This leads to an expression for a_f of

$$\left(\frac{\theta_H}{1-\theta_H}\right)^z\left(\frac{\theta_D/z}{1-\theta_D}\right)$$

This model is more complicated when the anions adsorbed are of different basicity, say, y and z. The foregoing argument indicates that adsorption of anions of basicity, say z, means that this is, in effect, grouping the amino groups into groups of z at will. If this be accepted, then adsorption of n_1 anions of basicity z means that there are $N - zn_1$ amino groups remaining to be neutralized. These can be disposed at will in groups of y, and hence the number of ways the n_2 molecules can be arranged will be

$$\frac{y^{n_2}\left(\frac{N-n_1 z}{y}\right)!}{n_2!\left(\frac{N-n_1 z}{y}-n_2\right)!}$$

If the n_2 molecules are introduced followed by the n_1 of basicity z, then the expression for $g(n_2)$ becomes

$$\frac{z^{n_1}\left(\frac{N-n_2 y}{z}\right)!}{n_1!\left(\frac{N-n_2 y}{z}-n_1\right)!}$$

In these formulas it has been tacitly assumed that the adsorptions of the two anions are behaving quite independently and that the effect of the introduction of the first type is merely to reduce the number of "sites" that may be at the disposal of the second type. Such a position must inevitably be derived from the apparent ability of the amino groups to be grouped at will according to the basicity of the anions. For the computation of the total combinatory formula, the number of sites occupied by the first anion must be treated as a constant. This will give

$$g(n_1)g(n_2) = \frac{z^{n_1}y^{n_2}(A/y)!(B/z)!}{n_1!n_2!\left(\frac{A}{y}-n_1\right)!\left(\frac{B}{z}-n_2\right)!} \tag{7}$$

where $A = N - n_1 z$; $B = N - n_2 y$.

This equation leads to the expressions

$$\frac{1}{z}\frac{\theta_1}{1-\theta_1-\theta_2} \quad \text{and} \quad \frac{1}{y}\frac{\theta_2}{1-\theta_1-\theta_2}$$

for the activities of the anions of basicities z and y respectively.

As discussed previously, the procedure adopted here is not a rigid one in terms of a point lattice. It does have the advantage, however, of yielding manageable expressions for the activities of the ions.

It is felt that this discussion and derivation underline the fact that the choice of a statistical model upon which the base calculations concerning some practical nonideal system is to some extent arbitrary. It must be judged chiefly by its ability to yield self-consistent results when applied to experimental data.

The expression for the affinity of a dye of basicity z may be written

$$-\Delta\mu^0_{HzD} = RT\log\left(\frac{\theta_H}{1-\theta_H}\right)^z\left(\frac{\theta_D}{1-\theta_D}\right) - RT\log[H]^z[D] - RT\log z \tag{8}$$

or, if two dyes are present,

$$-\Delta\mu^0_{HzD} = RT\log\left(\frac{\theta_H}{1-\theta_H}\right)^z\left(\frac{\theta_D}{1-\theta_D-\theta_A}\right) - RT\log[H]^z[D] - RT\log z \tag{9}$$

An analogous equation holds for $-\Delta\mu^0_{HyA}$. Subtraction of these equations then gives

$$-\Delta\mu^0_{HzD} - (-\Delta\mu^0_{HyA}) = RT\log\frac{\theta_D}{\theta_A} - RT\log\frac{[D]}{[A]} - RT\log\frac{z}{y} + RT\log\left[\frac{1}{[H]}\left(\frac{\theta_H}{1-\theta_H}\right)\right]^{z-y} \quad (10)$$

This equation can now be used to describe the desorption of one dye by an inorganic ion. The simplest manner in which to do this is to desorb under conditions in which the fiber is virtually saturated with hydrogen ions (i.e., $\theta_H \backsim 1$, in which case $\theta_A + \theta_D \backsim 1$ from the stoichiometry and there is no need to determine experimentally the quantity of the inorganic ion on the fiber since θ_A may be approximated to $1 - \theta_D$). The equation as it stands cannot be readily evaluated because of the behavior of the last term on the right-hand side, for as $\theta_H \to 1$, $\theta_H/1 - \theta_H \to \infty$. However, the condition of saturation described cannot be achieved mathematically unless the concentrations of the ions in the bath $\to \infty$, and hence, if the equation is to have any meaning, this term must tend to a limit. The existence of this can be seen by considering a dyebath containing the dye acids in a fixed ratio and letting the concentration of each be increased so that the ratio of the concentration, $[D]/[A]$, is constant. Under such conditions the ratio θ_D/θ_A remains constant. In the limit, as $[H] \to \infty$, the term

$$\log\frac{1}{[H]}\cdot\left(\frac{\theta_H}{1-\theta_H}\right)$$

must also tend to a limit. To evaluate this it is necessary to introduce a nonthermodynamical assumption that the ions may be treated individually, i.e.,

$$\Delta\mu^0_{HzD} = z\cdot\Delta\mu^0_H + \Delta\mu^0_D$$
$$\Delta\mu^0_{HyA} = y\cdot\Delta\mu^0_H + \Delta\mu^0_A$$

This assumption allows values of $\Delta\mu^0_D$ consistent with the results from other methods to be calculated for many dyes. The value of this limit can be deduced from the adsorption of a simple acid such as HCl when we have

$$-(\Delta\mu^0_H + \Delta\mu^0_{C1}) = RT\log\frac{1}{[H]}\cdot\left(\frac{\theta_H}{1-\theta_H}\right) + RT\log\frac{1}{[C1]}\cdot\left(\frac{\theta_{C1}}{1-\theta_{C1}}\right) \quad (11)$$

This must hold for all values of $[H]$ and $[C1]$ from zero to infinity and hence we may take limits, i.e.,

$$\text{Lim. R.H.S.} = -(\Delta\mu^0_H + \Delta\mu^0_{C1})$$

That is,

$$\lim_{[H]\to\infty} RT\log\frac{1}{[H]}\cdot\left(\frac{\theta_H}{1-\theta_H}\right) + \lim_{[C1]\to\infty} RT\log\frac{1}{[C1]}\cdot\left(\frac{\theta_{C1}}{1-\theta_{C1}}\right) = -(\Delta\mu^0_H + \Delta\mu^0_{C1}) \quad (12)$$

(since the limit of the sum is equal to the sum of limits) and, since it is assumed that the ions behave independently, these limits equal $-\Delta\mu^0_H$ and $-\Delta\mu^0_{C1}$ respectively. Hence equation 10 becomes

$$-\{(\Delta\mu^0_D - \Delta\mu^0_A) + (z-y)\Delta\mu^0_H\} = RT\log\frac{\theta_D}{\theta_A}\cdot\frac{[A]}{[D]} - (z-y)\Delta\mu^0_H - RT\log\frac{z}{y}$$

or

$$-(\Delta\mu^0_D - \Delta\mu^0_A) = RT\log\frac{\theta_D}{\theta_A}\cdot\frac{[A]}{[D]} - RT\log\frac{z}{y} \quad (13)$$

The result would have followed immediately from equation 10 if the independence of the ions had been assumed. Equation 13 is then suitable to calculate affinity differences between two ions. As mentioned earlier, it is usual to work under conditions such that the sites are approximately saturated; i.e., θ_A is replaced by $1 - \theta_D$.

$$-(\Delta\mu^0_D - \Delta\mu^0_A) = RT\log(\theta_D/1-\theta_D) - RT\log[D]/[A] - RT\log(z/y) \quad (14)$$

This is the equation employed in calculating the affinities of acid dyes from the results of desorption experiments described in the next section.

3. *Determination of Affinities*

The technique employed was similar to that of McGrew and Schneider. Nylon (5 g) was dyed for 3 hr at 85°C, using a 50:1 liquor ratio from a bath containing the acid whose anions were to be

used in the desorption and the amount of dye required to give the requisite fractional saturation. After dyeing was complete the fiber was treated for a further 3 hr in a bath containing sufficient of the same acid to give a *p*H of 3.2 in order to ensure that the dyeing was level. The fiber was removed, rinsed, and dried.

A 0.5-g sample of the dyed fiber was desorbed in 25 cc of liquor containing the sodium salt of the appropriate mineral acid and sufficient of that acid to produce a *p*H of 3.2. (Under these conditions, hydrogen ions were present in excess of the number required to produce complete ionization of the amine sites.) This experiment was carried out in an apparatus which consisted of a U-tube (Figure 4). The fiber was put into one arm, which was then sealed by a rubber bung; the other arm was connected to the system which ultimately connected the apparatus to the air and vacuum line alternately. By such a technique the liquid was sucked backward and forward through the fiber plug, thereby enabling the dye to be desorbed rapidly from the fiber. After 20 min the fiber was removed and replaced by another sample from the same stock; this second sample was treated in the desorbing liquor for some 20 min. Such a technique enabled the dyed fiber to be brought to equilibrium quickly with the external liquor without the necessity of redistribution of the dye throughout the fiber during the desorbing process. At the end of desorption the liquor was removed and the concentration of dye measured optically by means of a Unicam S. P. 600 spectrophotometer. The amount of dye on the batch of fiber was also estimated optically, the details being given previously. Two separate series of experiments were carried out with chloride and sulfate ions. Since these are mono- and dibasic ions respectively, it was thought that the results would enable equation 14 to be tested. Using the amine group titer as the saturation value, the fractional saturation was calculated and hence the affinity was found by substitution of the relevant quantities.

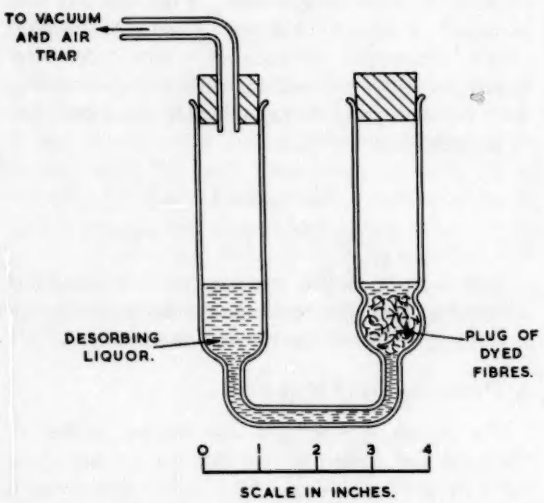


Fig. 4. Sketch of desorption apparatus.

Results and Discussion

The detailed experimental data are given in the appendix. In view of the results on stoichiometry given earlier, the fiber used in these experiments was dyed to such a strength that the fractional saturations were for the most part of the order of 0.8 or less, based on the amine group titer. It was felt that the use of the lower saturations reduced the ambiguity which might arise from the differences in saturation values between dyes described earlier and the use of the amine titer throughout only introduced a small error. The error is indeed small since the affinities are weighted numerically almost entirely by the term

$$RT \log \frac{[D]}{[A]},$$

the magnitude of

$$RT \log \left(\frac{\theta_D}{1 - \theta_D} \right)$$

being on average about 40 times smaller. Variations in the latter make little difference to the value of the affinity, which may therefore be regarded as a measure of the property of the dye toward desorption by inorganic ions. The average values of the affinities of the dyes are given in Table III, columns 4 and 5 referring to the experiments using chloride and sulfate ions.

The range of affinities given in column 4 is relatively large (3 kg-cal) and is of such an order that there is a difference of 100 in the concentration of dye desorbed from, say Solway Blue A and Naphthalene Red J. Comparison between the values using sulfate and chloride ions show the former to be substantially higher by as much as 2 kg-cal. This difference is stressed when the amounts of dye desorbed

TABLE III. Affinities Measured by Desorption at 75°C

Dye	(2) Basicity	(3) Color Index Number	(4) Affinity in Kg-Cal/M by Desorption with Chloride	(5) Sulfate	(6) Bisulfate	(7) Affinity Difference, Chloride-Bisulfate
Solway Blue A	2	—	−4.67	−6.80	−3.93	−0.74
Naphthalene Fast Orange 2G	2	27	−5.00	−6.41	−3.54	−1.46
Tartrazine N	3	640	−5.01	−6.54	−3.67	−1.34
Solway Blue BN	2	1054	−5.05	−7.18	−4.31	−0.74
Azogeranine 2G	2	31	−5.11	—	—	—
Lissamine Fast Yellow 2G	2	639	−5.31	−7.31	−4.44	−0.87
Lissamine Red 6B	2	57	−5.37	−7.39	−4.52	−0.85
Naphthalene Orange G	1	151	−5.82	−7.33	−4.46	−1.36
Naphthalene Scarlet 4R	3	185	−5.88	—	—	—
Naphthalene Orange RO	1	161	−6.03	−7.80	−4.93	−1.10
Naphthalene Orange I	1	150	−6.17	−7.80	−4.93	−1.24
Lissamine Red 7BP	2	—	−6.62	−8.54	−5.67	−0.75
Naphthalene Red EA	2	182	−6.52	—	—	—
Naphthalene Red J	1	176	−7.66	—	—	—

by both ions are compared, chloride desorbing about 10 times more than sulfate. In this respect nylon differed from wool, from which the amounts desorbed by both ions were comparable. On this basis sodium chloride should act as a better leveling agent for nylon than does sodium sulfate.

This difference in behavior can be explained to a large extent if it is assumed that the HSO_4^- ion is responsible for desorption rather than the divalent SO_4^{--} ion. This would mean that the active concentration of desorbing ion in solution would be less than the concentration of SO_4^{--} ion by a factor of approximately 30 (using a dissociation constant for the reaction $HSO_4^- \rightarrow H^+ + SO_4^{--}$ of 2×10^{-2} and assuming that the concentration of SO_4^{--} is unaffected by the desorption because of the large excess of sodium sulfate present).

On this hypothesis, the affinities calculated on the basis of the SO_4^{--} ion must be reduced (numerically) by 2.35 kg-cal. If this is the mechanism of desorption, however, it is necessary to make allowance for the difference of basicity in the first term of the affinity equation. With these modifications the affinities are shown in column 6 of Table III. It can be seen that these affinities are numerically smaller than those obtained by desorption with chloride (average difference = − 1.04 kg-cal). It is tempting to attribute the difference to the difference of affinity between Cl^- and HSO_4^- ions, but the amount of experimental evidence on this point is insufficient for any definite conclusions to be drawn, although this difference is of a comparable magnitude to the different affinities attributed to the chloride and sulfate ions when these are adsorbed on wool. This difference is 0.90 kg-cal. It seems, therefore, that the sulfate ion cannot be readily accommodated. This is not unexpected since it is a very small one and carries two charges. This point is brought out when a crude calculation is made of the distance between amino groups in the fiber. It is assumed for this purpose that all the amino groups are in the amorphous regions of the fiber; this has been suggested by the American workers and must arise from the fact that if the nylon molecular chains were to terminate in a crystalline region then the essential symmetry and close-packed nature of that region would be upset. Further, it is difficult to see how it can be otherwise in view of the stoichiometric relationship and the lack of alteration of X-ray pattern of the dyed fiber when compared to that of the undyed. This simple calculation gives a value for the distance between neighboring amino groups as about 30 A. Thus the small sulfate ion could not easily be attached to two sites, as could the very much larger dye anion. In wool, where the distances between amino groups is as low as 12 A, accommodation of the sulfate ions is not so difficult and the sulfate ion is readily capable of desorbing dye anions.

This assumption of the importance of the bisulfate ion in desorption received confirmation from the comparison of the titration curves of nylon with hydrochloric and sulfuric acids. The former was determined by Lemin and is reproduced in Figure 5, along with that for sulfuric acid as determined in the present work. The curves were produced by equilibrating nylon with solutions of acid and titrating

the residual acid. The difference in acid concentration before and after equilibration then gave the uptake of acid. For the low concentrations, direct titration was not possible and the amount of combined acid was determined from changes in the *p*H of the liquor. The difference is quite marked for, whereas the curve for hydrochloric acid gave an inflection corresponding to the amine end titer, the sulfuric acid experiments gave an inflection at a value 60% higher. This result must indicate that a substantial quantity of the acid adsorbed is as the bisulfate ion, although the fact that the inflection point is not twice the amine titer would indicate that some sulfate ions are also adsorbed.

The original concept in carrying out experiments using two ions of different valences (chloride and sulfate ions) in order to assess the validity of equation 14 had, therefore, to be abandoned. This equation is, however, considerably different from equation 15 of McGrew and Schneider for calculation of the affinity of a dibasic dye using the desorption technique.

$$-(\Delta\mu_D - 2\Delta\mu_{Cl}) = RT \log \left(\frac{\theta_D}{1-\theta_D}\right)^2 \cdot \left(\frac{\theta_D}{2-\theta_D}\right) - RT \log \frac{[D]}{[Cl]^2} \quad (15)$$

These authors reported affinity values of the range of mono- and dibasic dyes; the average affinity of the four monosulfonates which they studied was −6.3 kg-cal and of the four dibasic, −2.3 kg-cal, giving a difference of 4.0 kg-cal. This difference, due to the introduction of an extra sulfonic acid group into the molecule, seemed excessive, particularly in view of the greater molecular size of the disulfonated dyes which were studied and by comparison with the differences of affinity between mono- and dibasic dyes for wool. Evidence on this point is available from the work of Lemin and Vickerstaff [10], who measured an average affinity for wool of −5.9 kg-cal for 5 monobasic dyes at 60°C by free acid titration and desorption with chloride ion. Fern [4] measured the affinity of 24 dibasic dyes for wool at 60°C by desorption with sulfate ion and obtained an average value of −4.25 kg-cal. In order to make these results comparable it is necessary to allow for the difference between the affinities of the sulfate and chloride ions (0.9 kg-cal). If this figure is added to the average affinities of the disulfonated dyes, a value of −5.15 kg-cal is obtained as against −5.9 kg-cal for the monosulfonated dyes, corresponding to a difference of 0.75 kg-cal due to the extra sulfonic acid group. Further evidence on the effect of degree of sulfonation on affinity is available from an analysis of data determined by Speakman and Clegg due to Gilbert [6]. The equilibrium distribution of dye between wool and acid dyebaths containing varying amounts of sodium sulfate was investigated for a large number of acid dyes with varying degrees of sulfonation. Although it is not possible to obtain affinity values of the individual dyes because of the experimental conditions, Gilbert was able to calculate the difference in affinity between any two of the dye anions. Several of these dyes were identical except in degree of sulfonation, so that the effect on the affinity of a single sulfonic acid could be assessed. In the three cases reported, the dibasic dyes had affinities which were lower by 1.03, 0.86, and 0.96 kg-cal than those of the corresponding monobasic dyes. The average value of these three estimates is 0.95 kg-cal, which is in reasonable agreement with the value of 0.75 kg-cal derived from the results of Lemin and Vickerstaff and by Fern [4]. The large change of affinity of dyes for nylon with degree of sulfonation, which was reported by McGrew and Schneider, cannot therefore be reconciled with the data for wool. The significant difference between the work of McGrew and Schneider and that of Fern is that they used chloride ions to desorb disulfonated dyes, in contrast to Fern's use of sulfate ion.

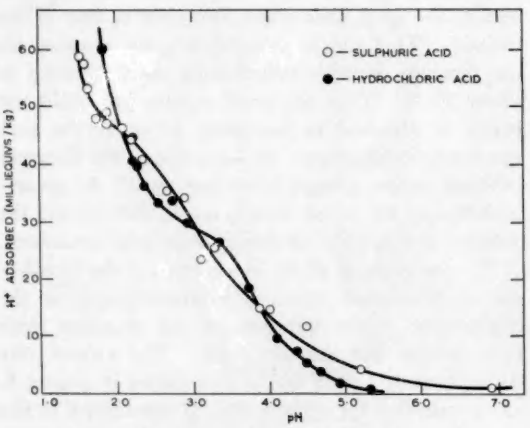


Fig. 5. Sulfuric and hydrochloric acid titration curves for nylon.

Evidence for the validity of equation 14 (i.e., a check on whether correct allowance has been made

TABLE IV

Dye	Basicity	Affinity Difference for a Change of One Sulfonic Acid in Kg-Cal/M (Equation 13)
Naphthalene Orange G	1	
Naphthalene Fast Orange SG	2	0.82
Naphthalene Red EA	2	
Naphthalene Scarlet 4R	3	0.64
Naphthalene Red J	1	
Naphthalene Red EA	2	1.14
	Average	0.87
Average value for wool	0.95 kg-cal (Speakman, Clegg, Gilbert)	
	0.75 kg-cal (Vickerstaff, Lemin, Fern)	

for the different basicities) is only available from a comparison of the type given above. This has been done in Table IV, where the affinities of three pairs of dyes are compared. In these, one dye of each pair differs from the other only by one sulfonic acid group. The affinity differences for this change are given.

The differences so obtained are in good agreement with those for the effects of changing a sulfonic acid group on the affinity of dyes for wool and therefore give confidence to the use of the formula (equation 14) derived in this work.

Finally, the effects of changing the hydrophobic character of the dye are of particular interest. Replacement of a benzene nucleus by a naphthalene gives an increase in affinity of as much as 1.5 kg-cal. This effect has been found with wool dyes by Gilbert and is suggestive of the idea that the main attractive forces between the dye and the fiber are nonpolar in character. Such a point of view has been put forward by other workers and is discussed in detail by Derbyshire and Peters [2]. It seems possible, therefore, that any structural change which increases the hydrophobic nature or polarizability of the dye increases its affinity for the fiber. Some results illustrating this are summarized in Table V.

TABLE V

Dye	Affinity (kg-cal/M)	Difference in Affinities
Naphthalene Orange G (benzene deriv.)	5.82	—
Naphthalene Red J (naphthalene deriv.)	7.66	1.84
Naphthalene Fast Orange 2G (benzene deriv.)	5.00	—
Naphthalene Red EA (naphthalene deriv.)	6.52	1.52

These differences of 1.84 and 1.52 may be compared with those of Gilbert of 1.35, 1.06, 1.51, and 1.46 for a series of dyes on wool. The effect is even noticeable on cellulose, where the difference in affinity between 1-benzoylaminoanthraquinone and 1-naphtholylaminoanthraquinone is some 1.23 kg-cal [16].

Conclusions

The work presented here confirms that adsorption of acid dyes by nylon is associated with the amino groups. It has been shown also that dyeing from concentrated dyebaths gives rise to overdyeing and the extent to which this occurs is characteristic of the dye. Overdyeing occurs to a greater extent, the greater the affinity of the dye and the smaller the number of sulfonic acid groups. Isotherms, in which the *p*H is kept constant and the dye concentration varied, indicate that the initial amounts of dye taken up by the fiber are attached to the amino groups. This point has been assumed in the determination of affinities of 12 dyes by the desorption method, fiber saturations being kept at 50%, or less, of the amine titer.

In order to determine the affinities of dyes of varying basicity a simple derivation of the thermodynamic formulas has been given. This formula has been used throughout and gives affinity results which are consistent and are analogous to those determined by other workers using wool, the justification for this choice of model being a comparison of the affinities of dyes with different numbers of sulfonic acid groups. The results obtained here are similar to those on wool.

A point of some interest in this connection is the difference in desorbing power observed between the chloride and sulfate ions. It is difficult to account for this difference unless it is assumed that the active concentration of the sulfate ion in the desorbing solutions is considerably lower than the amount of sulfate added. This has been explained assuming that the HSO_4^- ion is responsible for the desorption of dyes from nylon in contradistinction to desorption from wool, in which the sulfate ion is the active desorbing agent.

Appendix

Experimental Data

Affinities Measured by Desorption at 75°C with

Dye	Chloride [Cl] (molar)	Chloride $[D_s]$ (molar×10^5)	Chloride θ	Chloride $\Delta\mu_D-\Delta\mu_{Cl}$ (kg-cal/M)	Sulfate $[SO_4]$ (molar)	Sulfate $[D_s]$ (molar×10^5)	Sulfate θ	Sulfate $\Delta\mu_D-\Delta\mu_{SO_4}$ (kg-cal/M)
Solway Blue A	0.051	2.517		−4.38	0.0505	0.143		−6.49
	0.101	4.620	0.346	−4.44	0.1005	0.379	0.337	−6.84
	0.201	6.889		−4.64	0.2005	0.405		−7.08
	0.051	2.872		−4.62	0.0505	0.409		−6.52
	0.101	6.538	0.460	−4.52	0.1005	0.693	0.483	−6.64
	0.201	8.692		−4.80	0.2005	1.256		−6.70
	0.051	3.568		−4.72	0.0505	0.666		−6.73
	0.101	6.736	0.549	−4.76	0.1005	0.928	0.674	−6.98
	0.201	9.332		−5.03	0.2005	1.249		−7.26
							Ave.	−6.80
	0.051	2.733		−4.59				
	0.101	5.109	0.447	−4.63				
	0.201	8.053		−4.79				
			Ave.	−4.67				
Naphthalene Red J	0.051	0.025		−7.76				
	0.101	0.047	0.266	−7.64				
	0.201	0.106		−7.71				
	0.051	0.059		−7.54				
	0.101	0.109	0.383	−7.59				
	0.201	0.182		−7.71				
			Ave.	−7.66				
Naphthalene Fast Orange 2G	0.051	2.374		−4.93	0.0505	4.992		−6.30
	0.101	4.748	0.520	−4.92	0.0505	5.863	0.891	−6.15
	0.201	7.947		−5.03	0.1005	5.901		−6.65
					0.1005	7.092		−6.53
							Ave.	−6.41
	0.051	4.624		−4.92				
	0.101	8.321	0.677	−4.98				
	0.201	9.910		−5.35				
	0.101	7.848		−4.93				
	0.201	9.929	0.657	−5.24				
			Ave.	−5.00				
Tartrazine N	0.051	0.657		−4.99	0.0505	1.355		−6.06
	0.101	1.922	0.329	−4.71	0.0505	1.573		−5.97
	0.201	2.885		−4.90	0.1005	1.982	0.703	−6.27
					0.1005	2.312		−6.17
	0.051	1.013		−5.08				
	0.101	2.623	0.463	−4.89				
	0.201	3.799		−5.11	0.0505	1.827		−6.94
					0.0505	—		—
	0.051	1.602		−4.70	0.1005	2.624	0.926	−7.23
	0.101	2.421	0.443	−4.89	0.1005	3.023		−7.13
	0.201	3.307		−5.16			Ave.	−6.54
	0.101	1.932		−5.22				
	0.201	2.587	0.520	−5.50				
			Ave.	−5.01				

Appendix—Continued

Dye	Affinities Measured by Desorption at 75°C with Chloride: [Cl] (molar)	[D_s] (molar × 10^6)	θ	$\Delta\mu_D - \Delta\mu_{Cl}$ (kg-cal/M)	Sulfate: [SO_4] (molar)	[D_s] (molar × 10^6)	θ	$\Delta\mu_D - \Delta\mu_{SO_4}$ (kg-cal/M)
Solway Blue BN	0.051	1.331		−4.99	0.0505	0.188		−6.90
	0.101	2.490	0.403	−5.03	0.1005	0.236	0.426	−7.20
	0.201	4.289		−5.14	0.2005	0.357		−7.40
	0.051	2.404		−5.03	0.0505	0.329		−6.91
	0.101	4.766	0.563	−5.03	0.1005	0.433	0.574	−7.20
	0.201	6.739		−5.28	0.2005	0.632		−7.44
	0.051	3.647		−4.81	0.0505	0.448		−6.95
	0.101	5.755	0.586	−4.97	0.1005	0.642	0.654	−7.18
	0.201	7.864		−5.22	0.2005	0.912		−7.41
			Ave.	−5.05			Ave.	−7.18
Azogeranine 2G	0.051	0.507		−5.21				
	0.101	1.378	0.257	−4.98				
	0.201	2.888		−4.96				
	0.051	0.656		−5.40				
	0.101	2.013	0.374	−5.09				
	0.201	3.999		−5.09				
	0.051	1.040		−5.10				
	0.101	2.678	0.440	−5.08				
	0.201	4.595		−5.18				
	0.051	0.994		−5.15				
	0.101	1.781	0.358	−5.10				
	0.201	3.282		−5.03				
			Ave.	−5.11				
Lissamine Fast Yellow 2G	0.051	2.914		−4.84	0.0505	0.210		−7.09
	0.101	5.075	0.540	−4.92	0.1005	0.262	0.514	−7.41
	0.201	7.757		−5.11	0.2005	0.308		−7.75
	0.051	3.715		−5.22	0.0505	0.572		−7.04
	0.101	7.004	0.720	−5.24	0.1005	0.832	0.731	−7.25
	0.201	8.425		−5.60	0.2005	0.993		−7.60
	0.051	5.275		−5.38	0.0505	1.260		−6.89
	0.101	8.080	0.823	−5.56	0.1005	1.623	0.829	−7.20
	0.201	10.260		−5.88	0.2005	1.851		−7.56
			Ave.	−5.31			Ave.	−7.31
Lissamine Red 6B	0.051	0.653		−5.26	0.0505	0.100		−7.10
	0.101	1.182	0.323	−5.31	0.1005	0.116	0.346	−7.49
	0.201	1.670		−5.54	0.2005	0.160		−7.75
	0.051	0.785		−5.48	0.0505	0.176		−7.07
	0.101	1.674	0.443	−5.43	0.1005	0.207	0.466	−7.43
	0.201	2.397		−5.67	0.2005	0.271		−7.73
	0.051	1.609		−5.06	0.0505	0.216		−7.01
	0.101	2.851	0.474	−5.15	0.1005	0.285	0.497	−7.29
	0.201	3.598		−5.46	0.2005	0.354		−7.61
			Ave.	−5.37			Ave.	−7.39

Appendix—Continued

Dye	Affinities Measured by Desorption at 75°C with: Chloride [Cl] (molar)	Chloride $[D_s]$ (molar×10⁶)	Chloride θ	Chloride $\Delta\mu_D-\Delta\mu_{Cl}$ (kg-cal/M)	Sulfate $[SO_4]$ (molar)	Sulfate $[D_s]$ (molar×10⁶)	Sulfate θ	Sulfate $\Delta\mu_D-\Delta\mu\theta_{O_4}$ (kg-cal/M)
Naphthalene Orange G	0.051	0.861		−5.82	0.0505	0.322		−6.88
	0.101	1.574	0.414	−5.86	0.1005	0.314	0.389	−7.36
	0.201	2.606		−5.99	0.2005	0.413		−7.66
	0.051	1.858		−5.54	0.0505	0.549		−6.89
	0.101	3.536	0.506	−5.57	0.1005	0.586	0.523	−7.31
	0.201	5.000		−5.80	0.2005	0.616		−7.76
	0.051	2.094		−5.81	0.0505	0.740		−7.00
	0.101	3.313	0.634	−5.98	0.1005	0.870	0.634	−7.36
	0.201	5.952		−6.05	0.2005	1.008		−7.72
			Ave.	−5.82			Ave.	−7.33
Naphthalene Scarlet 4R	0.051	—		—				
	0.101	0.179	0.219	−5.93				
	0.201	0.528		−5.66				
	0.051	0.184		−6.07				
	0.101	0.988	0.410	−5.40				
	0.201	1.534		−5.55				
	0.051	0.469		−6.50				
	0.101	1.506	0.724	−6.01				
	0.201	3.311		−5.94				
			Ave.	−5.88				
Naphthalene Orange RO	0.051	0.787		−6.05	0.0505	0.252		−7.36
	0.101	1.384	0.491	−6.13	0.1005	0.301	0.517	−7.88
	0.201	2.544		−6.19	0.2005	0.326		−8.14
	0.051	1.343		−5.89	0.0505	—		—
	0.101	2.437	0.566	−5.95	0.1005	0.382	0.600	−7.79
	0.201	3.866		−6.11	0.2005	0.387		−8.25
	0.051	3.561		−5.70	0.0505	0.706		−7.18
	0.101	4.649	0.723	−5.98	0.1005	—	0.697	—
	0.201	6.447		−6.23	0.2005	0.842		−8.01
			Ave.	−6.03			Ave.	−7.80
Naphthalene Orange I	0.051	0.675		−6.13	0.0505	0.223		−7.28
	0.101	—	0.483	—	0.1005	0.238	0.457	−7.71
	0.201	2.309		−6.23	0.2005	0.268		−8.11
	0.051	0.935		−6.04	0.0505	0.246		−7.29
	0.101	1.627	0.531	−6.13	0.1005	0.273	0.543	−7.86
	0.201	2.946		−6.20	0.2005	0.299		−8.27
	0.051	1.404		−6.15	0.0505	—		—
	0.101	2.664	0.666	−6.18	0.1005	0.472	0.626	−7.72
	0.201	4.372		−6.32	0.2005	0.508		−8.14
			Ave.	−6.17			Ave.	−7.80

Appendix—Continued

Dye	Affinities Measured by Desorption at 75°C with Chloride: [Cl] (molar)	[D_s] (molar × 10^5)	θ	$\Delta\mu_D - \Delta\mu_{Cl}$ (kg-cal/M)	Sulfate: [SO_4] (molar)	[D_s] (molar × 10^5)	θ	$\Delta\mu_D - \Delta\mu_{SO_4}$ (kg-cal/M)
Lissamine Red 7BP	0.051	0.093		−6.57	0.0505	0.432		−8.55
	0.101	0.282	0.311	−6.32	0.0505	0.417	0.651	−8.60
	0.201	0.685		−6.14	0.1005	0.637		−8.79
					0.1005	1.464		−8.20
							Ave.	−8.54
	0.051	0.102		−6.76				
	0.101	0.311	0.389	−6.43				
	0.201	0.798		−6.27				
	0.051	0.265		−6.52				
	0.101	0.708	0.543	−6.31				
	0.201	1.279		−6.38				
			Ave.	−6.62				
Naphthalene Red EA	0.051	0.070		−7.23				
	0.101	0.295	0.474	−6.72				
	0.201	1.276		−6.28				
	0.051	0.313		−6.61				
	0.101	0.803	0.611	−6.41				
	0.201	1.982		−6.27				
	0.051	0.531		−6.47				
	0.101	1.194	0.691	−6.40				
	0.201	2.641		−6.32				
			Ave.	−6.52				

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Treatment of Wool Scouring Wastes with Colloidal Bentonite[1]

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Abstract

Results are presented of a laboratory-scale study to determine the effectiveness of various coagulants as supplementary additives in the conventional acid cracking of wool scouring wastes. It was observed that a dispersible-type bentonite produces a marked improvement in the extent of clarification of the waste effluent. In brief, the treatment involves first acidifying the scouring wastes with sulfuric acid to a *p*H level between 3 and 4 and then adding the required amount of bentonite as an aqueous dispersion. The amount of bentonite required depends upon the grease and suint content of the waste. A bentonite concentration of between 0.1 and 0.5% is generally sufficient. As an example, treatment of a standard waste with acid and bentonite removed as much as 96% of the grease, compared with removal of 67% with acid alone. The chemical oxygen demand was reduced by approximately 60% by the combination treatment, compared with 33% reduction with acid alone.

Introduction

Wool-scouring wastes result from the conventional aqueous cleaning of raw wool to render it suitable for processing. The spent liquors from scouring contain grease (more correctly, wax), suint salts (primarily water-soluble salts of organic acids), protein matter, fecal material, dirt, and vegetable matter removed from the raw wool, and in addition the soap or synthetic detergent and soda ash. Because of its high content of decomposable organic matter, which is extremely objectionable from the standpoint of stream pollution, disposal of scouring wastes represents an important problem of long standing. This situation is aggravated by the fact that the wool-scouring industry is concentrated in the heavily industrialized and populated New England states.

For the most part, treatment of scouring wastes is directed toward recovery of grease as a salable by-product. Abatement of stream pollution is a secondary factor, except in those few cases where purification of waste liquor is mandatory by law. It is estimated, however, that only slightly over a third of the scouring plants in this country operate grease-recovery systems. In this country the average annual production of wool grease is approximately 10 million lb, which represents 10 to 15% of the estimated total potential available [6].

There are two principal commercial methods of treating scouring wastes and recovering grease. These are the centrifugal process and the acid-cracking process. In addition, processes based upon the use of calcium chloride [5] or calcium hypochlorite [4] have been reported.

The centrifugal process is by far the most common. It is purely mechanical and employs high-speed centrifuges. It recovers a neutral (less than 1 to 2% free fatty acid) light-colored grease known as neutral degras, which commands a premium price. The clarified liquor from the centrifuge, containing suint, soap, and alkali, can be returned to the scouring bowls for further use. Centrifugal systems are employed primarily for production of high-quality grease. Such systems seldom recover more than 30% of the total grease of the wastes and remove practically none of the dissolved organic matter. Consequently, there is little improvement in the characteristics of the effluent responsible for polluting streams. Further chemical or biological treatment is necessary for satisfactory pollution abatement. According to a recent patent [2], the recovery of

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grease by centrifuging can be doubled by pretreating spent scouring liquors with about 4 to 6% of sodium chloride. An improved process [3] combining froth flotation and centrifugation has been reported recently in Australia, for which recovery of around 50% of the grease is claimed.

In the acid-cracking process the waste scouring emulsion is "cracked" by addition of sulfuric acid to bring the liquor to a *p*H of about 3.5. The grease and dirt are removed after they settle by gravity. The grease is then separated by filtration under heat and pressure. The over-all yield of grease is around 50% of the total present in the wastes. The grease produced, known as common degras, is somewhat dark in color and has an undesirably high fatty acid content, so that it brings a lower price (approximately three-fourths that of neutral degras).

Although acid cracking produces an effluent which is less objectionable from the standpoint of stream pollution than that resulting from a mechanical process, it still gives inadequate purification. A high residual organic content and high acidity remain. With increasing use of synthetic detergents in scouring, a further problem arises in acid cracking; emulsions stabilized by synthetic detergents are not easily broken by conventional acid treatment.

This paper presents results of a laboratory-scale investigation of use of a dispersible-type bentonite as an inexpensive supplementary coagulant in the acid-cracking process to improve grease removal.

Experimental

For our investigation of methods for treating wool-scouring wastes, we needed a supply of scouring-waste liquor of constant composition. Dependence upon a local commercial plant for samples proved impractical because of wide daily variations in properties of the waste.

In order to control these variations for our initial studies, we developed a miniature scouring apparatus. It consists essentially of four 8-liter stainless-steel beakers, which served as the scouring bowls, mounted in a constant-temperature bath with provisions for mechanical agitation of the wool and for expressing the scouring liquors.

The operation consisted of feeding 4 separate 150-g samples of raw wool through the first bowl and squeeze roll, then through the second bowl, and so on through the system. The first and second bowls each held 4 liters of a solution containing 0.3% sodium carbonate and 0.1% sodium oleate. The final two bowls functioned as rinsing bowls. All bowls were maintained at 130°F and the time of immersion in each bowl was 2 min. The spent scouring solution from the first bowl, which contained the highest concentration of grease, suint, and dirt, was used for experimental purposes in the investigation of various treating methods. The liquors were allowed to stand for an hour before decanting to remove the heavier dirt particles. They were used the same day they were prepared.

The raw wool employed as a standard was a large lot of California-grown fine-grade wool. The entire lot was opened and blended in a laboratory-scale opener [7] and stored at 35°F to minimize aging effects which might alter the waste. This lot had a grease content of 12.4%, a suint content of 11.8%, and a dirt content of 10.3%.

In the coagulation procedure, the freshly prepared raw waste was cooled to room temperature before aliquots were taken for treatment by various experimental methods. The treated waste was allowed to stand with occasional stirring for 1 hr and then centrifuged to separate the precipitated sludge from the clarified liquor.

In most instances, the extent of clarification of the raw waste by the various treatments investigated was estimated by measurement of turbidity. This measurement was made with a Beckman DU spectrophotometer, and the results were expressed as absorbancy ($\log_{10} To/T$, where To is the transmittancy of water and T is the transmittancy of the clarified waste). A wavelength of 1000 mμ was employed in order to minimize the effect of the absorbance due to the colored substances in suint.

In some instances a more complete analysis was carried out by determining the grease content, total solids, chemical oxygen demand (C. O. D.) by the permanganate method, and total nitrogen. These analyses were carried out in a manner prescribed by the American Public Health Association [1].

Results and Discussion

In a preliminary survey of possible aids for the coagulation of wool-scouring wastes, including various mineral clays, starches, natural gums, and synthetic high polymers, both ionic and nonionic, it was observed that colloidal bentonite when added to an acidified scouring waste produced a marked improvement in clarification.

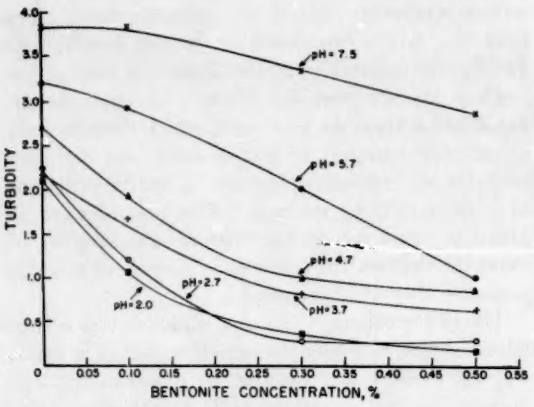

Fig. 1. Effect of bentonite concentration on turbidity of clarified waste effluent at various *p*H levels.

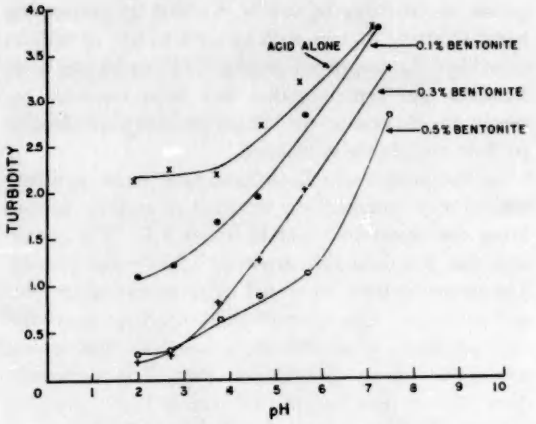

Fig. 2. Effect of *p*H on turbidity of clarified waste effluent at various bentonite concentrations. (Replot of data in Figure 1.)

The results obtained by treating the standard waste with bentonite over a range of *p*H levels are shown in Figure 1. They are presented again in Figure 2 as a function of *p*H at several bentonite-concentration levels. These results show that the effectiveness of bentonite as a coagulant increases with decreasing *p*H until an optimum level is reached near *p*H 3.5. The optimum concentration of bentonite at this *p*H level is around 0.3%. (In the present paper concentration in g/100 ml of waste is referred to as per cent.) These values will vary somewhat, especially the optimum bentonite concentration, depending upon the nature of the waste treated. It should be noted that with acid alone the further addition of acid below *p*H 4 has little improving effect on degree of clarification (Figure 2). In the conventional acid-cracking process, the treatment is generally carried out at a *p*H of approximately 3.5.

The bentonite used as a standard material in this investigation was a quick-dispersing pelleted product, KWK Volclay [2] (obtained from the American Colloid Company), mined in the Black Hills region and composed mainly of montmorillonite. In the treatment of the scouring waste, bentonite was added as a 5% aqueous dispersion. The waste was acidified first before treatment with bentonite. This was carried out by adding the required amount of sulfuric acid as a 6 *N* solution.

The titration curve for the standard waste is shown in Figure 3. These results were obtained by adding the indicated amount of 6 *N* sulfuric acid to 100 ml of waste and measuring the corresponding *p*H. In the *p*H range between 3 and 8, the *p*H of the acidified waste was a nearly linear function of the acid concentration.

Under the optimum condition of treatment, the combination bentonite-acid treatment produces a voluminous precipitated sludge and a nearly optically clear light-yellow clarified effluent. This is in contrast to acid treatment alone, which produces a highly turbid light-brown effluent. The clear effluent can be

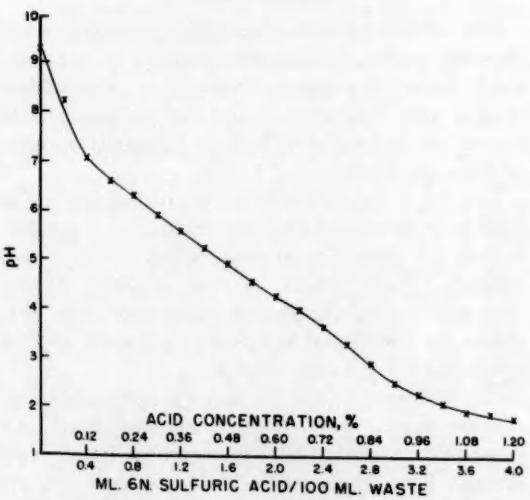

Fig. 3. Titration curve of standard scouring waste.

[2] Mention of specific products does not imply endorsement by the Department of Agriculture over others of a similar nature not mentioned.

TABLE I. Analytical Results of Treating Scouring Waste With Acid and Bentonite

Treatment	pH	Turbidity Absorbance (units)	Grease (ppm)	C. O. D. (ppm)	Total Solids (ppm)	Total Nitrogen (ppm)
Raw waste	9.5	4.5	18,000	6,887	44,400	920
0.5% Bentonite treatment	9.2	3.6	10,000	5,662	35,000	730
Reduction, %			55	18	21	21
Acid treatment	3.4	2.6	6,100	5,305	29,400	580
Reduction, %			66	33	34	37
Acid plus 0.1% bentonite	3.4	1.5	4,300	4,015	25,800	510
Reduction, %			76	42	42	45
Acid plus 0.2% bentonite	3.4	0.63	3,800	3,465	23,300	450
Reduction, %			79	50	47	51
Acid plus 0.3% bentonite	3.4	0.26	2,000	2,920	22,500	430
Reduction, %			89	58	49	53
Acid plus 0.4% bentonite	3.4	0.16	1,400	2,745	21,800	420
Reduction, %			92	60	51	54
Acid plus 0.5% bentonite	3.4	0.11	700	2,632	21,300	410
Reduction, %			96	62	52	55
Acid plus 0.6% bentonite	3.4	0.09	800	2,507	20,800	390
Reduction, %			96	64	53	58

separated from the waste after treatment with acid and bentonite by filtration or by centrifugation.

The analytical results of treating our standard scouring waste with acid and bentonite are summarized in Table I.

Under optimum conditions the combination acid-bentonite treatment removes up to 96% of the original grease in the waste, compared with a removal of 67% with acid alone. The combination treatment lowers the chemical oxygen demand by over 60% compared with acid treatment alone, which removes only 33% of the original C. O. D.

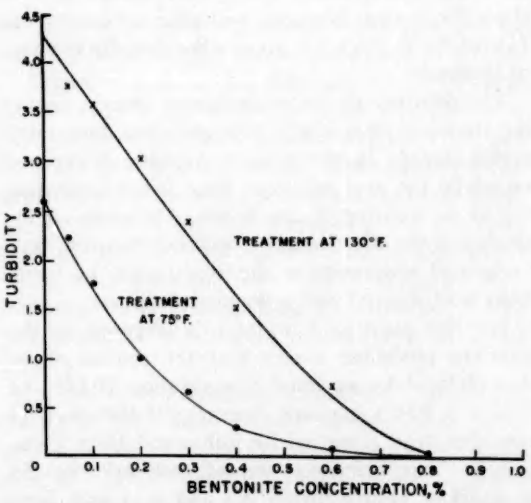

Fig. 4. Effect of temperature of bentonite-acid treatment on turbidity of clarified waste effluent.

The data in Table I show that there is a fairly close correlation between the per cent reduction in C. O. D. and the per cent reduction in nitrogen. The nitrogen in the scouring waste originates, for the most part, in the water-soluble suint of raw wool. It also should be pointed out that there is a nearly linear correlation between the turbidity and the total solids content of the various samples. The relationship between turbidity and grease content deviates considerably from linearity, but this is to be expected because of the contribution to turbidity from the suspended dirt.

In the standard coagulation procedure described above, the raw waste was first cooled to room temperature before treatment with acid and bentonite. The effect of temperature on extent of clarification is shown in Figure 4. This series of experiments was carried out at the optimum pH level of about 3.5. The treatment at the elevated temperature was carried out by taking the freshly prepared raw waste directly from the scouring bowl at a temperature of 130°F and adding the desired amount of acid and bentonite. Approximately twice the concentration of bentonite is required for effective clarification at the higher temperature as at room temperature. The higher amount of bentonite required is a reflection in part of the rather poor coagulation efficiency of the acid at the higher temperature. A much more compact sludge was obtained by treatment at the higher temperature. This sludge sedimented quite rapidly, giving a final volume of sediment approximately one-half that observed for treatment at the lower temperature.

A study was made also of the effectiveness of a number of commercially available water-dispersible colloidal clays from several sources as supplementary coagulants in the acid cracking of scouring wastes. The following clays (supplied by Baroid Sales Division, National Lead Company) were included in this study: (a) Zeogel, an attapulgite mined in Florida; (b) Baroco, a calcium bentonite mined in Texas; (c) M H Bentonite, a magnesium silicate mined in California; and (d) Bentonite A, a montmorillonite mined in California. In addition, a sample of colloidal silica (supplied by Dow Corning Corporation) and two representative nondispersible clays, fuller's earth and kaolinite, were included in the study for comparative purposes.

The reduction in turbidity of the standard scouring waste with increasing concentrations of these additives is shown in Figure 5. In this series of experiments, the waste was acidified wtih sulfuric acid to a *p*H level of about 3.5 in all cases before addition of the indicated materials.

The dispersible clays and the sample of silica were nearly equally effective as coagulants for the acid-treated waste. The montmorillonite mined in California was somewhat more effective than the other clays.

The nonswelling or nondispersible clays, fuller's earth and kaolinite, were found to be relatively ineffective as aids to coagulation.

The comparative effectiveness on an equal-weight basis of bentonite (KWK Volclay), alum, and ferric sulfate (reagent grade chemicals were used) as coagulants under acid conditions for the standard scouring waste is shown in Figure 6. On the abscissa scale of this plot, the concentration of alum is expressed as grams of $Al_2(SO_4)_3 \cdot 18\ H_2O$ per 100 ml of waste and in the case of ferric sulfate as grams of $Fe_2(SO_4)_3 \cdot 9\ H_2O$ per 100 ml. In treating the waste with alum and ferric sulfate, the indicated amounts of these chemicals were first added and then the *p*H adjusted to 3.5 by the addition of sulfuric acid. In the case of bentonite, the waste was acidified before adding the clay.

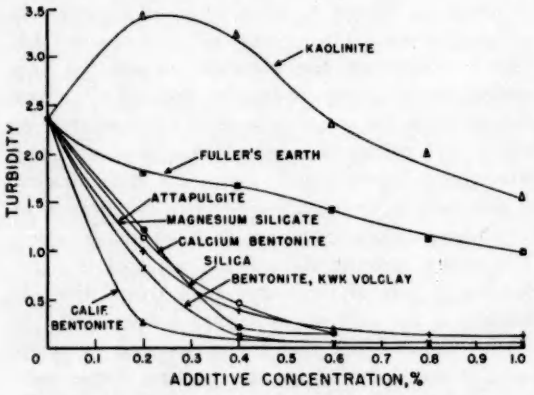

Fig. 5. Relative effectiveness of various colloidal and non-colloidal clays and silica as coagulants for scouring waste at *p*H 3.5.

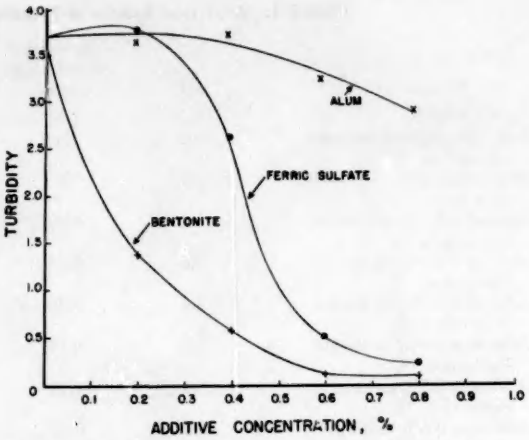

Fig. 6. Relative effectiveness of alum, ferric sulfate, and bentonite as coagulants for scouring waste at *p*H 3.5.

Alum is relatively ineffective as a supplementary additive in the treatment of our standard waste. At the lower concentration levels, ferric sulfate is relatively ineffective; however, at higher concentrations (above 0.4 to 0.6%) it approaches the effectiveness of bentonite.

The difficulty in the acid-cracking process resulting from use of synthetic detergents has been mentioned above. In recent years synthetic detergents, especially the nonionic type, have found increasing use in the scouring of raw wools. Therefore we investigated the effectiveness of our experimental bentonite-acid treatment in the coagulation of waste from wool scoured with a nonionic detergent.

For this purpose, a waste was prepared by the standard procedure except that the sodium oleate was replaced by an equal concentration (0.1%) of Triton X-100, a nonionic detergent of the alkylaryl polyether type (supplied by Rohm and Haas Company). This waste was treated with sulfuric acid to a *p*H of approximately 3.5 and then with bentonite (KWK Volclay). The comparative results

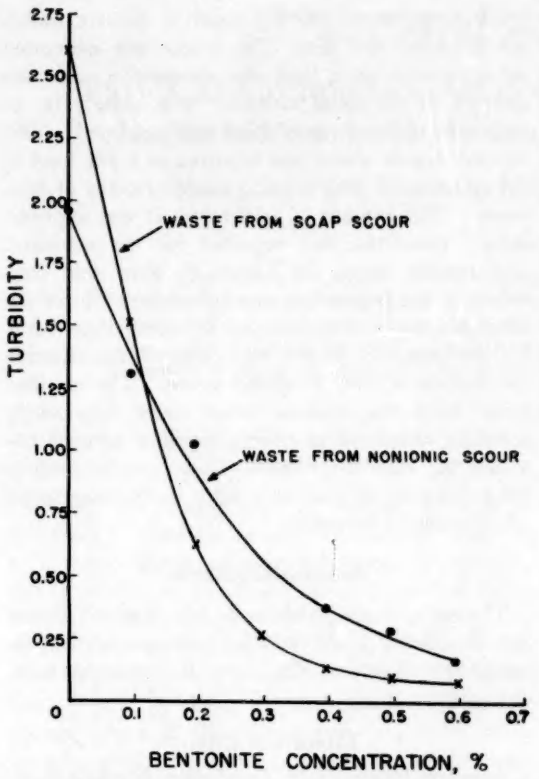

Fig. 7. Comparison of results of bentonite-acid treatment of wastes prepared by scouring with soap and soda ash and by scouring with nonionic detergent and soda ash.

for this waste and the standard waste prepared by scouring with sodium oleate are shown in Figure 7. These data show that with acid treatment alone the turbidity of the clarified effluent from the nonionic-prepared waste was somewhat lower than that from the soap-prepared waste. This difference can be attributed to the added turbidity of the precipitated sodium oleate in the soap-prepared waste. In spite of this initial lower turbidity, the nonionic-prepared waste was somewhat more difficult to clarify with bentonite, as is evidenced by the crossover in the two curves at a bentonite concentration of about 0.1%.

In the experimental work described up to this point, the data were obtained by treating a waste prepared from a lot of California-grown fine-grade raw wool which was used as a standard. To determine the effectiveness of the combination bentonite acid-treating procedure on waste from different wool, a lot of California-grown New Zealand merino wool was selected. This wool was scoured by the standard procedure, and the resultant waste was treated by the usual method. In adjusting its *p*H to a level of 3.5, only three-fourths of the amount of acid used previously in the treatment of the standard waste was required.

A comparison between the results obtained with the waste prepared from merino wool and the standard waste is shown in Figure 8. The difference in behavior of these two wastes is rather pronounced. On treatment with acid alone, the turbidity of the clarified effluent from the merino waste was considerably lower than that from the standard waste. Furthermore, only 0.1% bentonite was required for effective clarification of the merino waste as compared to approximately 0.3 to 0.4% for the standard.

In an attempt to determine the reason for this difference, an analysis of the grease, suint, and dirt

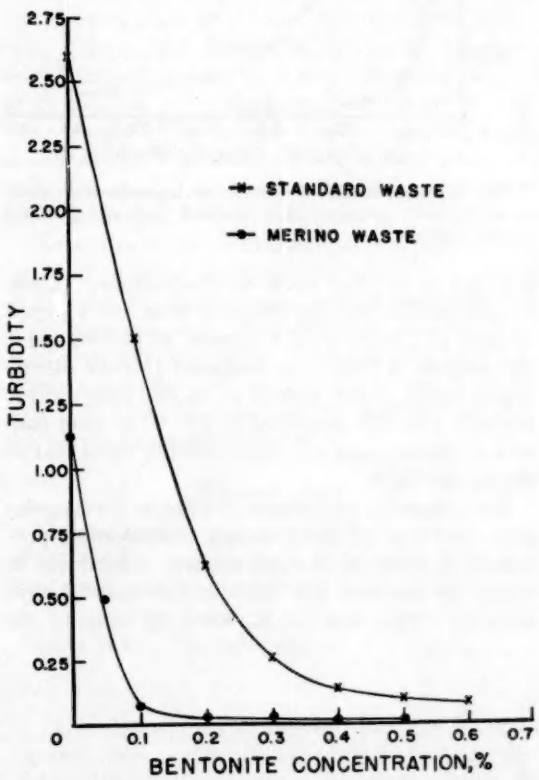

Fig. 8. Comparison of results of bentonite-acid treatment of wastes prepared from standard wool and merino wool.

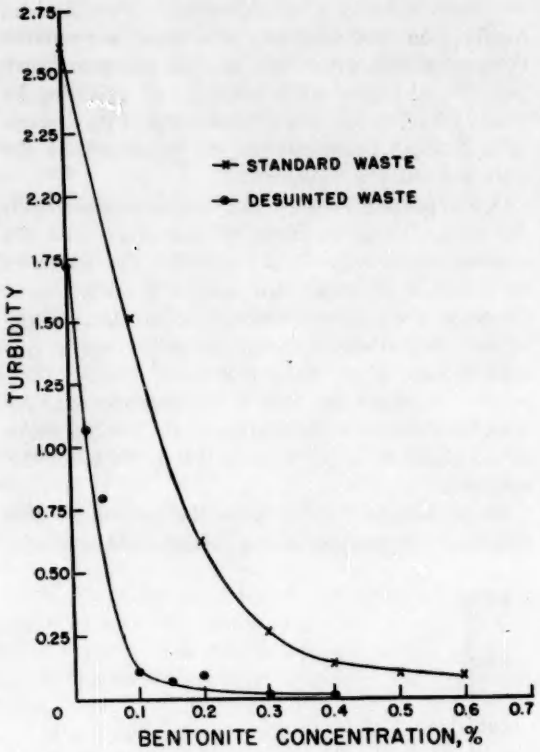

Fig. 9. Comparison of results of bentonite-acid treatment of wastes prepared from standard wool and desuinted standard wool.

contents of the two wools was carried out. These results showed that the standard wool had a grease content of 12.4%, a suint content of 11.8%, and a dirt content of 10.3%, as compared (for the merino wool) with a grease content of 14.5%, suint content of 6.4%, and dirt content of 11.1%. The suint content of the standard was approximately twice that of the merino wool.

To explore the importance of suint in the coagulation efficiency of the bentonite acid-treating procedure, a series of experiments was carried out in which the standard raw wool was desuinted before scouring. This was accomplished by steeping the wool in lukewarm (90°F) water to remove water-soluble suint and dirt. The water was expressed with squeeze rolls, and the desuinted wool was scoured in the usual manner. The same ratio of raw wool to scouring solution was employed. This desuinted-wool waste was adjusted to a *p*H level of 3.5 and treated with varying concentrations of bentonite. The amount of acid required was approximately two-fifths that required for the standard. The results, shown in Figure 9, show that considerably less bentonite (approximately 0.1% for the desuinted waste compared to approximately 0.3% for the standard waste) was required for effective clarification of the desuinted waste. The clarified waste from the desuinted-wool waste was nearly colorless compared to the light-yellow effluent obtained for standard waste. These results confirm the importance of suint as a factor in the coagulation effectiveness of bentonite.

Acknowledgments

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Cellulose Studies

Part XX. Comparison of Polymolecularity of Celluloses Degraded by Acid Hydrolysis and by Alkali Aging[1]

Yves Siegwart,[2] Ludwig Rebenfeld,[3] and Eugene Pacsu[4]

Abstract

Experimental molecular weight distribution curves are presented for two degraded cellulosic materials. Both samples were degraded to approximately the same average degree of polymerization, the first by the normal viscose-aging process and the other by acid-catalyzed hydrolysis. Comparison of these curves reveals a fundamental difference in the distribution of chain lengths in these two degraded materials.

Introduction

During the manufacture of viscose rayon it is necessary to degrade the starting cellulosic material to a lower degree of polymerization. Industrially this is carried out as a base-catalyzed reaction by allowing cellulose impregnated with sodium hydroxide to stand for a period of time while exposed to atmospheric oxygen in a constant-temperature room. Undoubtedly oxidation of the cellulose is an important phase of the degradation procedure, being superimposed on the simple shortening of the polyglucose chains. It is now generally accepted that in order to prepare a proper "viscose dope," not only the average degree of polymerization but also the molecular weight distribution of the cellulose are important factors.

The molecular weight distribution of degraded cellulose has been extensively studied. Particular attention has been paid to acid-degraded celluloses and some molecular weight distribution curves have been cited as evidence for acid-sensitive linkages which have served as the basis for the weak-link theory of cellulose structure [6, 8]. Recently, degradation of cellulose has been shown to take place by ultrasonic radiation [9], and molecular weight distribution curves for cellulose degraded ultrasonically have been reported by Page [7]. Thomas and Alexander [11] have ultrasonically degraded cellulose nitrate and have compared the molecular weight distribution curves with cellulose degraded by alkaline aging. These workers concluded that alkaline aging yields a more heteromolecular product than ultrasonic radiation. Sihtola and Kaila [10] compared the polymolecularity of wood-pulp cellulose at various stages of purification and degradation and concluded that when depolymerization takes place at the aging stage, a more uniform product is obtained than when depolymerization is allowed to take place at previous purification steps.

Since it is of interest to compare the polymolecularity of cellulosic materials degraded to the same D.P. value by alkaline aging and by acid-catalyzed hydrolysis, this paper presents the experimental molecular weight distribution curves of two such cellulosic materials. Both these products were degraded to a D.P. value which is approximately that suitable for viscose rayon manufacture.

Experimental

The starting cellulosic material was cellulose sheets (D.P. = 940) derived from wood pulp which are used for rayon manufacture and which were donated to us by the American Viscose Corporation of Marcus Hook, Pennsylvania.

Acid Degradation

Three 6-g portions of the cellulose were placed in separate flasks with 100 ml of 1 *N* HCl and hydrolyzed at 60°C. The times of hydrolysis were 70, 130, and 190 min. After the prescribed hydrolysis

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[2] Textile Research Institute Visiting Scientist. Present address, Société de la Viscose Suisse, Heerbrugg, St. Gallen, Switzerland.

[3] Staff Member, Textile Research Institute.

[4] Research Associate, Textile Research Institute, and Professor of Chemistry, Princeton University.

TABLE I. Acid and Alkaline Degradation of Wood Pulp Cellulose

Acid Degradation			Alkaline Degradation		
Sample	Time of Hydrolysis (min)	D.P.	Sample	Time of Hydrolysis (hr)	D.P.
1	70	485	4	22	742
2	130	418	5	43	558
3	190	345	6	65	435

time the samples were filtered, washed with water, and dried in an oven at 55°C.

Alkaline Degradation

Twenty grams of the cellulose were cut up in small pieces and placed into 300 ml of 6 *N* sodium hydroxide solution at 27°C and allowed to soak for a period of 90 min with occasional stirring. After this time the alkali cellulose was filtered and the resulting cake was crumbled into small bits. The degradation was allowed to take place by exposing this material to atmospheric oxygen at room temperature, which varied during the time of the experiment from 24° to 27°C. Approximately one-third of the bulk material was removed at the end of 22, 43, and 65 hr, the time being measured from the filtration of the excess sodium hydroxide. The samples were washed with large quantities of water, filtered, and dried in an oven at 55°C.

D.P. Determination

The degree of polymerization of the six degraded samples was determined by the viscosity technique described in detail by Mehta and Pacsu [5] with the exception that cupriethylenediamine instead of cuprammonium hydroxide was used as the solvent. Data are tabulated in Table I; samples 2 and 6 were used for the molecular weight distribution experiments.

Nitration and Fractionation

The two degraded samples (2 and 6) were nitrated by the mixed-acid method set forth by Brownsett and Davidson [2] and modified by Davis [4] of the Hercules Powder Company. This method yields a nitrocellulose of approximately 13% nitrogen content as analyzed by the method described by Busch and Schneider [3], using the organic reagent nitron.

A 1% solution in acetone of each cellulose nitrate was prepared and any undissolved material was filtered off. Fractional precipitation was used as the means of establishing the molecular weight distribution of the two products. Fractions of the cellulose nitrate were collected by the successive addition of water, and the degree of polymerization of each fraction was determined by the viscosity technique. This method is described in detail by Mehta and Pacsu [6], and the experimental results are tabulated in Tables II and III.

TABLE II. Fractionation of Cellulose Nitrate Prepared from Cellulose Hydrolyzed for 130 Min in 1 *N* HCl at 60°C

Fraction	Weight (g)	Per Cent	Total Per Cent	Cumulative Per Cent ($IP \times 10^2$)	D.P.
15	0.208	4.30	4.30	2.15	28
14	0.151	3.12	7.42	5.86	76
13	0.189	3.91	11.33	9.38	106
12	0.212	4.38	15.71	13.52	147
11	0.289	5.97	21.68	18.70	201
10	0.180	3.72	25.40	23.54	221
9	0.193	3.96	29.36	27.38	249
8	0.241	4.98	34.34	31.85	282
7	0.185	3.82	38.16	36.25	313
1*d*	0.245	5.06	43.22	40.69	319
6	0.361	7.47	50.69	46.96	344
5	0.380	7.84	58.53	54.61	385
4	0.203	4.20	62.73	60.63	405
3	0.221	4.57	67.30	65.02	438
1*c*	0.306	6.32	73.62	70.46	536
2	0.357	7.38	81.00	77.31	567
1*b*	0.246	5.08	86.08	83.54	664
1*a*	0.675	13.92	100.00	93.02	886

TABLE III. Fractionation of Cellulose Nitrate Prepared from Cellulose Degraded for 65 Hr by Alkali Aging at Room Temperature

Fraction	Weight (g)	Per Cent	Total Per Cent	Cumulative Per Cent ($IP \times 10^2$)	D.P.
14	0.185	4.13	4.13	2.06	56
13	0.172	3.84	7.97	6.05	106
12	0.194	4.33	12.30	10.14	164
11	0.290	6.48	18.78	15.54	217
10	0.159	3.55	22.33	20.56	259
9	0.162	3.62	25.95	24.14	294
8	0.220	4.91	30.86	28.40	327
7	0.183	4.09	34.95	32.90	356
6	0.266	5.94	40.89	37.92	374
1*d*	0.182	4.07	44.96	42.92	397
5	0.420	9.39	54.35	49.66	474
4	0.234	5.23	59.58	56.96	526
3	0.614	13.70	73.28	66.43	589
2	0.363	8.12	81.40	77.34	628
1*c*	0.277	6.19	87.59	84.50	690
1*b*	0.212	4.73	92.32	89.96	865
1*a*	0.344	7.68	100.00	96.16	1165

In both the acid- and alkaline-degraded materials the large first fraction was refractionated into four subfractions. A plot of $IP \times 10^2$ (cumulative per cent) vs. degree of polymerization yields the integral distribution curve. Graphical differentiation of this curve yields the slope at any point, and plotting this slope vs. the degree of polymerization results in a mass distribution curve, shown in Figures 1 and 2.

Discussion

Although the average degree of polymerization of the two degraded celluloses is for all practical purposes the same, it is obvious that the molecular weight distribution is radically different. The acid-degraded material shows a mass-distribution curve similar to that which has frequently been observed by other workers [1, 6], with a maximum slightly lower than the average degree of polymerization and a pronounced positive skewness. The molecular weight distribution shown by the alkaline-degraded material is interesting in that it shows two clearly distinct maxima, one at a degree of polymerization value of 400 and the other at a value of approximately 600. The double peak in the alkaline material

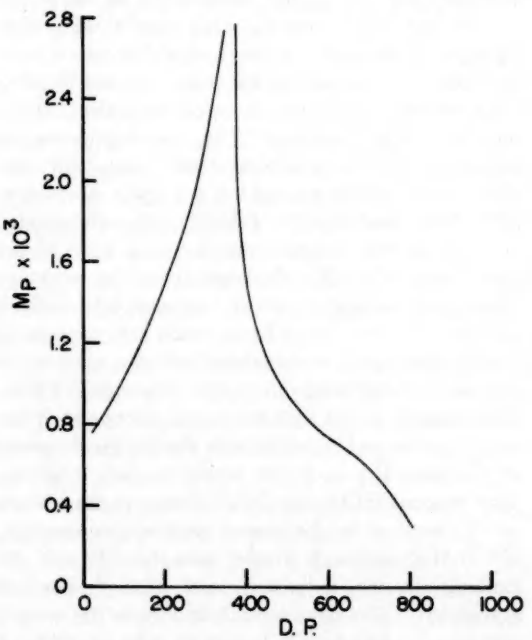

Fig. 1. Mass distribution curve for material derived from acid-hydrolyzed cellulose (Table II).

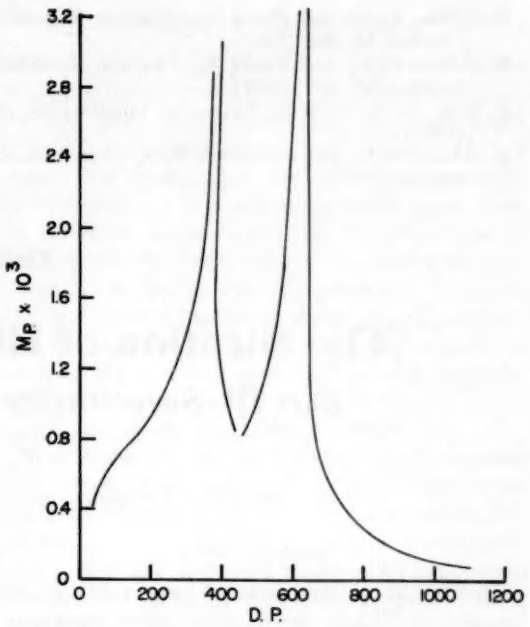

Fig. 2. Mass distribution curve for material derived from alkali-aged cellulose (Table III).

is undoubtedly significant and must be considered in proposing a mechanism for the alkaline aging process. It suggests that a definite periodicity of points vulnerable to alkali attack exists and further suggests that not all of these vulnerable points are available for attack. Susceptible sites for alkali degradation within the micelles or crystallites may be protected from reaction by their position in the inner core of these ordered regions. It is not possible from these data to propose the distance between alkali-vulnerable sites except to limit the upper value of such a distance to 400 D.P. units. The influence of a double-peak molecular weight distribution curve on the physical properties of the resulting rayon filaments, compared with a single-peak molecular weight distribution curve, should be given due consideration.

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The Sorption of HCl by Textile Fibers[1]

Part III. Sorption by Proteins and by Nylon

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Introduction

In Part II of this series of papers [4] on the sorption of HCl by textile fibers, some results obtained with nylon and other polyamide fibers were reported. Since then two papers dealing with the sorption of HCl by similar substances have come to our attention. As these have a bearing on the work we reported and on some of the work carried on since then in our laboratory, they merit comment in the light of our results. One of these, by Seehof and Benson [7], deals with the interaction of polar gases, including HCl, with solid proteins and some simple organic compounds, including nylon. The other is a thesis by Peterson [5] and deals specifically with the sorption of NH_3 and HCl by nylon and insulin. It will be convenient to review these two papers separately. In discussing the paper by Seehof and Benson, it will be necessary to refer to some of their earlier work [1, 2].

Residual HCl Content

Of the various observations made by Seehof and Benson [7], one of the most significant is the amount of HCl which remains on the absorbent after desorption, and which the authors claim is held irreversibly. In most cases they found this to be equivalent to the combining capacity of the basic amino acid constituents. Exceptions to this correlation were casein zinc insulin and silk fibroin, which retained larger amounts of HCl than those expected from their arginine, histidine, and lysine contents. Seehof and Benson attributed this to the very slow desorption process in materials having a close-packed structure, and they cite the high residual HCl content in nylon as an example, since the fibrous nylon retained 2.73 mM of HCl per gram,[2] compared with 0.18 mM for the amorphous nylon. Our results with wool, nylon, and silk also indicate a slow desorption process, but we obtained no evidence that the residual HCl tended to a constant value equivalent to the basic amino acid content. The most significant observation in this connection is that made with oxidized wool, which retained a negligible amount of HCl after desorption (4, Table I) although the HCl retained by the untreated wool was a little higher than the 0.91 mM calculated from the arginine, lysine, and histidine content. It would be difficult also, on the basis of the basic amino acid content, to explain the results we obtained with the wool which had been treated with dinitrofluorbenzene (DNFB). This reagent reacts with the amino groups of lysine and arginine and possibly with the imidazole group of histidine [6], and one would expect, therefore, little residual HCl in the DNB wool; yet the amount of HCl retained by the treated wool was appreciable, 0.99 mM/g, although smaller than the 1.39 mM remaining on the untreated wool after 5 days of evacuation. The same remark applies to the treated silk sample, which still had 0.42 mM of HCl, as

[1] This paper is designated N.R.C. No. 3688.

[2] All sorption figures will be given in millimoles (mM) HCl per gram of adsorbent.

compared with 0.77 mM for the untreated sample, after 15 days' evacuation.

It might be pointed out that the discrepancy found by Seehof and Benson for zinc insulin is perhaps only an apparent one. Sanger [6] has calculated that each molecule of insulin (mol. wt. = 12,000) has four free amino groups, two due to glycine and two due to phenylalanine. These would increase the combining capacity of the insulin by 0.33 mM/g. This, added to the 1.05 mM given by Seehof and Benson for the arginine + histidine + lysine content, gives 1.38, which agrees well with the 1.35 mM residual HCl found.

Although our results do not seem to be in accord with the conclusions reached by Seehof and Benson, they do not necessarily indicate the absence of compound formation between HCl and the basic amino acid residues. If compounds are formed, their vapor or dissociation pressure is sufficiently high to result in a decomposition of the compound when evacuated. It is quite possible that our evacuation process was more complete than that existing in the experiments of Seehof and Benson. This is indicated by the results with nylon. Whereas Seehof and Benson give a residual HCl content of 2.73 mM for the fibrous nylon, we were able to obtain as low a figure as 0.27 mM after 11 days' desorption.

We have also investigated the uptake of HCl by glycylglycine and other compounds of similar nature (unpublished results), and we obtained a much higher sorption than that reported by Seehof and Benson, namely, 0.90 M of HCl per M of glycylglycine, as against 0.63 M obtained by Seehof and Benson. It should be noted in this connection that the amount of irreversibly bound HCl they found for glycine was only 0.10 mM/g, whereas this amino acid contains 13.5 mM amino groups per gram.

If a definite compound is formed between the amino groups and HCl, it is also difficult to explain the absence of isobars in the desorption curves which Benson and Seehof obtained in their investigation of egg albumin [1, 2]. The sorption isobars indicate a compound corresponding to 0.95 mM HCl per gram of protein at a pressure of 0.11 cm; yet the desorption curve from a pressure of 0.40 cm shows no break except perhaps at a very small pressure (0.01 cm). The observation that the amount of HCl bound depends on the pressure up to 2 cm is difficult to reconcile with the formation of a compound having a dissociation pressure of around 1 mm.

Sorption of HCl by Nylon

The experiments of Peterson [5] on the sorption of HCl by nylon were carried out with a sample of undrawn nylon, whereas most of our tests were made with ordinary commercially drawn nylon. In this respect our results are not strictly comparable. Nevertheless, we have also observed in some cases the maximum in the sorption vs. time curves noted by Peterson, but this was much smaller for the drawn nylon than for the undrawn sample we tested. The latter gave a maximum which was 6.3% higher than the final equilibrium value, a value which is of the same order as that noted by Peterson, while the drawn nylon gave a maximum which was only ~ 2% higher than the final equilibrium value.

We did not observe, as Peterson did, that samples of nylon containing residual HCl had a sticky feeling when removed from the sorption apparatus, but we did observe in some cases that the nylon fibers, where they had been tied together for suspension purposes, had stuck to each other so as to form a solid brittle mass, although the remaining portions of the fibers appeared unchanged. These portions of fibers were dissolved in formic acid, and the viscosity of the solution was determined. This indicated that no significant degradation had taken place. The fused portions were too small for viscosity measurements. We have not yet determined under what conditions this fusion of the filaments takes place, but it did not occur in all the tests.

In view of the remarks made earlier in this paper regarding residual HCl, it is interesting to note that Peterson was able to remove all the HCl from some of his samples by heating at 90° while evacuating the system. The sample of nylon so treated was found to have practically the same strength and elongation as the original fiber. Experiments which we have carried out on nylon under tension indicate that the change taking place in the nylon on HCl sorption is dependent to a great extent on the tension. Since Peterson held his nylon yarn wound on a glass frame, his results were affected by the tension which is bound to develop in the yarn. Indeed, Peterson observed that the glass frame on which his yarn was wound was crushed in one instance by the tension of the yarn. This tension is due to the tendency of the yarn to contract when it sorbs HCl. Peterson observed that this contraction is followed by an elongation in the case of undrawn nylon. With drawn nylon we observed only a contraction on

HCl sorption, and this was followed by a further, though smaller, contraction on evacuation. The contraction was accompanied by a pronounced swelling of the filament. These experiments will be dealt with in a separate communication.

We have not made a thorough investigation by X-rays of the changes produced in the nylon by the HCl, but the diagrams we obtained show definitely that the orientation of the macromolecular chains is destroyed by the HCl. This must mean that hydrogen bonds have been broken. We have additional evidence for this from infrared studies which will be reported later. The rupture of H-bonds would evidently explain the shortening of the fiber, since the segments of the chain set free would tend to assume a more random distribution to increase the entropy. The lengthening of the undrawn fiber observed by Peterson might possibly be due to an orientation effect produced by the HCl after a certain amount has been sorbed. This can be expected if the HCl forms hydrogen bonds with the amide linkages, but dipole-dipole interaction may also result in a certain degree of orientation since, under the influence of HCl, two neighboring amide groups would tend to occupy parallel positions.

Our experiments with nylon are not sufficiently complete to allow us to determine whether the isotherms follow the Freundlich type of equation, as we observed with our earlier work with wool [3], but it is interesting to note that if one plots Peterson's results at 0° and 20°C, the isotherms follow rather the Langmuir equation, whereas the results obtained at −78.9°C follow neither equation. The curves obtained by plotting Peterson's results in this way show no discontinuity at low pressures, thus indicating that the steps noted by Peterson when one and two molecules of HCl were sorbed per amide group were more apparent than real, a conclusion which Peterson arrived at from a study of an isobar at 1.0 cm pressure.

Peterson also carried out some experiments with zinc insulin and observed, as Benson and Seehof had, that some HCl remains permanently bound on desorption. However he notes that the amount so bound is strongly temperature dependent. This suggests that the amount of HCl retained by the protein is diffusion controlled and is not in the nature of a definite compound. This is further shown by the low energy change involved.

From the fact that the insulin, for any given pressure, sorbs much less HCl than nylon does, Peterson concludes that the sorption process is different for the two substances. If the HCl sorption is due mainly to the peptide linkage, as we claim, there should be no essential difference in the nature of the sorption by insulin and that by nylon, and any difference in amount sorbed must be due merely to a difference in the accessibility of the peptide linkages, if we take into account the difference in peptide group content. The heats of reaction also indicate that there is no essential difference between HCl sorption by nylon and HCl sorption by a protein. From the 0° and 20° isotherms obtained by Peterson, we have calculated the isosteric heat of sorption to be − 14 kg-cal/mole, when 12.6 mM of HCl are sorbed, and −12.5 kg-cal for 11.5 mM sorption. From our own results with nylon we get −8.8 kg-cal for 10.9 mM sorbed, which is in fair agreement with Peterson's results since there is a decreasing heat of sorption as the quantity sorbed decreases. The figures for insulin are not sufficiently complete to allow the calculation of the heat of sorption, but we may take wool as an example of a protein and use our earlier results [3], which give a ΔH of −7.0 kg-cal for 3.9 mM of HCl sorbed and −7.5 kg-cal when 6.0 mM of HCl are sorbed. There is nothing in these figures to indicate that the sorption of HCl by nylon is different in nature from that by wool, and therefore from that of any other protein.

Summary

The sorption of HCl by nylon and by certain proteins is discussed in the light of some recent results, particularly with reference to the amount of HCl retained by the adsorbent on desorption. The changes produced in nylon as the result of HCl sorption are also mentioned, and the heat of sorption has been calculated.

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Observations on Certain Fluorescent Spots in Raw Cotton Associated with the Growth of Microorganisms

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Abstract

Evidence is presented which indicates that certain fluorescent spots observed in raw cotton under ultraviolet light are associated with the prior growth of microorganisms on the fiber. A striking and characteristic type of spot which fluoresces bright greenish-yellow was noted frequently in classers' samples from the 1954 cotton crop grown around Yuma, Arizona, and Brownsville, Texas. It was also, but less frequently, noted in samples from other regions of Texas and occasionally in samples from other states. Spots of this particular type have been shown to be associated with growth on the fiber of the fungus *Aspergillus flavus*, three principal lines of evidence having been obtained: (1) the very common occurrence of *A. flavus* in the fluorescent spots; (2) the production of a fluorescence of similar appearance by *A. flavus* growing on cotton fiber in pure culture; and (3) the similarity of the fluorescent substances from field- and *A. flavus*-incubated fiber in chromatographic behavior and absorption spectrum. The fluorescent fiber in commercial samples exhibited abnormally high swelling in alkali and decreased strength.

A white-fluorescent spot, less striking and less easily recognized than the above, has been found to be associated with certain isolates of the fungus *Alternaria* sp. Several other common types of microbial growth on cotton prior to harvest were not accompanied by distinct differences in fluorescence as compared with uninfected fiber, indicating that under the conditions here employed ultraviolet examination is not a general tool capable of detecting all of the types of microbial infection present in commercial cotton.

Spots which Fluoresce Bright Greenish-Yellow ("BGY" Spots) Associated with the Fungus *Aspergillus Flavus*

Preliminary Observations

In November of 1953, a sample of unginned cotton fiber and bolls which had been collected from plants at Blythe, California, was sent to the Department at Beltsville with a request for diagnosis of the cause of a yellowish stain and low strength in the fiber. The yellow spots in the affected fiber exhibited a brilliant greenish-yellow fluorescence under ultraviolet light ("Mineralight," Model V41, 0.25 amp, peak intensity at 2537 Å). Subsequently, several samples of ginned fiber were received from other sources and were noted to have brightly fluorescent spots in them which resembled in color the fluorescence in the Blythe sample. Since no information pertinent to the problem could be located in the literature, an investigation was undertaken.

The plants from which the Blythe sample had been collected were stated to have been approximately 6 ft tall and grown together into a dense mass of vegetation in the field, a circumstance leading to shading of the lower bolls and to the occurrence of a high humidity around them. The stain was found principally in the fiber of the lower bolls, where it was said to have appeared at the time of boll opening. Many of the locks were incompletely fluffed and the fiber could be pulled off the seed very easily. Often the basal portion of the lock was compact, while the remainder of the lock was more or less fluffed. The fluorescent color frequently extended to the base of the lint fibers; i.e., it was not localized on the surface of the lock. The carpels were free from the gross distortion and sticking of the fiber to the inner carpel wall which are characteristic results of attack

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by various types of insects during the developmental period of the boll. No insects were present and no insect punctures or other signs of insect activity could be detected by either macroscopic or microscopic observation.

In commercial-ginned lint samples, a fluorescence of similar appearance was noted, this fluorescence occurring in discrete spots usually comprised of 10 to 100 mg of fiber. Such spots were described at first in laboratory notes as "bright greenish-yellow" spots in reference to their color under ultraviolet light and later simply by the abbreviation "BGY" spots, a designation also used frequently in the present report. Microscopic examination revealed that BGY spots had a good deal of fungal mycelium in them and that the fiber was visibly damaged. In addition, the fiber exhibited abnormally high swelling in alkali (Table I), an indication of damage to the outer fiber wall, and decreased strength. Strength comparisons between fluorescent and nonfluorescent fiber in classers' samples from a wide variety of locations, using the Pressley breaker with 1-mm gap jaws, regularly resulted in lower values for the fluorescent fiber, the observed differences on a percentage basis in a series of such samples being as follows: 42, 21, 25, 15, 20, 21, 27, 28, 45, 25, 31, 39, 19, 25, 27, 7, 40, 34, and 28. In some cases the true differences may have been greater than these recorded values as a result of the combing out of damaged fiber from the fluorescent material during preparation of the bundle for breaking.

TABLE I. Alkali-Swollen Width of Fibers from Bright Greenish-Yellow Fluorescent Spots in Comparison with the Same for Nonfluorescent Fibers from the Same Samples

(Each figure in the table is an average derived from a single measurement on each of 100 fibers, swollen and measured in 18% NaOH. Data considered to indicate damaged condition of the outer wall of the fluorescent fibers.)

Source of Sample and Designation	Width in Microns: Fluorescent Fibers	Width in Microns: Nonfluorescent Fibers	L. S. $D._{0.05}$
Mr. Stuart Evans			
Blythe sample	35.6	25.4	0.8
Mr. Edwin Jennings			
41746	31.4	25.3	0.4
43029	30.7	25.0	0.4
"Calif. Cotton"	29.0	24.9	0.3
Mr. C. F. Rainwater			
Sample 1	30.7	25.3	0.3
Dr. J. P. Elting			
Sample 3	32.3	24.7	0.5
Sample 4	32.7	24.8	0.4
Mr. K. T. Louis			
Sample 1	32.0	24.7	1.0

Identification of Microorganisms Present in BGY Fiber

In the case of the Blythe sample, examination of the material as received disclosed definite evidence of the presence of a fungus of the genus *Aspergillus;* this fungus was subsequently identified as *Aspergillus flavus. Aspergillus* spore heads were present on the fiber, on the outer surfaces of the bolls, and on the pedicels or boll stalks; when the spore heads were transferred to an agar medium and allowed to grow, they produced cultures which were identified, at first tentatively, as *A. flavus.* An isolate obtained from the fiber was sent to Miss D. Fennell, an authority on the identification of *Aspergilli* who was located at that time at the U.S.D.A. Peoria laboratory, and its identity was confirmed. This was our culture #144, to which Miss Fennell assigned the Peoria number A 5501. Additional evidence on the identity of other cultures here designated as *A. flavus* was obtained at Beltsville by comparisons with a key culture of the species, *A. flavus* NRRL No. 482, which had been employed in the original description of the species [13, p. 263–266]. The seeds of the Blythe sample were internally infected with *A. flavus.* After surface sterilization with sodium hypochlorite and washing in sterile water, the seeds were cut apart with a sterile scalpel and the fragments planted on water agar. In the course of a few days, most of these fragments were covered with a heavy growth of *A. flavus.* The seeds were not distinctly fluorescent internally, either before or after this incubation.

Numerous BGY-fluorescent ginned-fiber samples from many sources were examined to determine the identity of any microorganisms which might be present on them. All observations were made after a period of approximately 72 hr incubation of the fluorescent fiber on water agar. Such incubation was necessary as a result of the fact that the fruiting structures of any fungi present had been knocked off the fiber during ginning or other mechanical flexing so that identification by direct examination was not possible. This situation occurs with many fungal infections of cotton fiber, and it has been found necessary to incubate the fiber in small tufts on a layer of water agar (2% agar) in Petri dishes to allow any fungi present to develop new fruiting structures so that they may be recognized [6]. The

method is known to require cautious interpretation, for the reason that the microorganisms which grow sufficiently in the laboratory to enable identification in this manner may include, at least in part, types which were present on the original sample only in the form of a surface contamination of spores.

Some of the first samples examined in respect to their microbial population were received from Mr. Edwin Jennings of Anderson, Clayton, and Company, Houston, Texas. During the course of a visit at Beltsville in December, 1953, Mr. Jennings indicated that he had seen fluorescent spots in samples from baled cotton. Subsequently, eight fiber samples were forwarded by him to Beltsville at our request. It was noted that the rather numerous fluorescent spots in these samples were similar in appearance to those in the Blythe sample. From various of the Anderson-Clayton samples, 25 small tufts were incubated as described above. *A. flavus* was noted in abundance on 12 of them and subsequently was isolated from 24 of them. In cultures of 14 of the isolates, hard blackish-brown sclerotia developed, similar to those described for *A. flavus* [13]. The bales from which the samples had been taken came from California, probably originating in the crop of 1953.

Subsequently, water-agar incubation and microscopic examination for identification of microorganisms present were carried out on fluorescent fiber from samples received from Mr. K. T. Louis of Otto Goedecke, Inc. (7 samples, coming from Arizona, Arkansas, and Texas), Dr. J. P. Elting of Kendall Mills (4 samples, from Arizona), Mr. O. Niles of Calcot, Ltd. (1 California sample), Miss Dorothy Nickerson (1 sample from Brownsville, Texas, and 1 other sample of unknown origin), and Mr. C. F. Rainwater (1 sample, from San Benito, Texas). Although several fungi were noted on these samples, the commonest and most abundant were *A. flavus, A. niger,* and *Rhizopus* sp. Later, a series of 1954 classers' samples was made available through the courtesy of Miss Dorothy Nickerson of the Standards and Testing Branch of the U.S.D.A. Agricultural Marketing Service, Washington, D. C. When tufts of fiber from 116 BGY spots (representing 116 bales) of the Nickerson samples were incubated and examined, 111 of them had a growth of *A. flavus,* 81 had *A. niger,* and 67 had *Rhizopus* sp., with various other fungi being present on a smaller proportion of the samples. From the several above-described observations, it seemed reasonable to suspect that one or more of these three fungi might be associated in some way with the production of BGY spots in nature.

Pure Culture Tests for the Production of Fluorescent Fiber

The mycological examinations described above were recognized to be of less than decisive significance as a means of certainly determining the causal agent or agents of the BGY fluorescence and were accordingly supplemented by two further types of experiments in order to ascertain this point more definitely. The first of these was to grow in pure culture on cotton fiber those organisms which had been identified on the natural BGY fiber and to examine the incubated fiber for fluorescence. The second was to compare the properties of the fluorescent materials from such incubated fiber with the properties of the fluorescent material from natural BGY spots.

The appearance of the yellow stain in the Blythe sample was said to have occurred at the time of boll opening. This observation suggested that the growth of fungi on BGY fiber in the field probably took place principally before the fiber had ever dried out. This supposition was made more plausible by previous evidence to the effect that none of the three fungi observed commonly on BGY spots has been found capable of more than limited growth on the ordinary dry cotton fiber of commerce [11]. Accordingly, pure-culture incubations were carried out on undried fiber (Figure 1). The method of incubation was as follows. Unopened or slightly cracked bolls harvested from greenhouse-grown plants were brought to the laboratory on the day on which they were to be used. They were surface-sterilized by flaming with 95% ethyl alcohol. Each boll was placed into a sterile Petri dish and pried open with a sterile scalpel. Then each boll was transferred to a sterile 100-ml beaker containing 10 ml of water, the beaker being set into a sterile cotton-plugged 1-qt fruit jar containing 100 ml of sterile distilled water. The fiber was inoculated by brushing spores onto the outer surface of the lock with a sterile camel's hair brush. In experiments with *Alternaria,* inoculation was carried out with a transfer needle instead of a brush. The bolls were then incubated for 14 days in the dark at about 30°C, although later experiments showed that with *A. flavus* about half this time was adequate for the production of bright fluorescence.

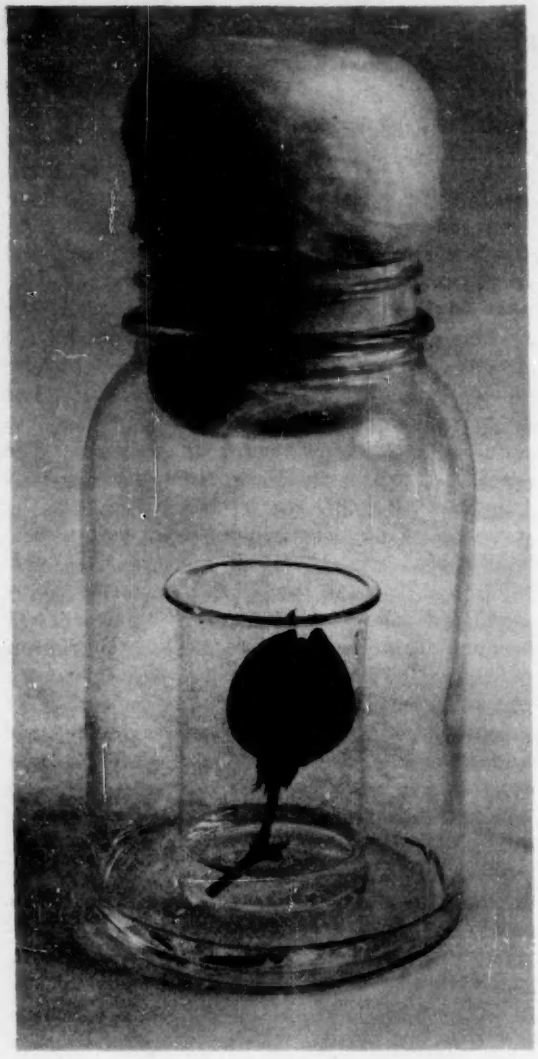

Fig. 1. Culture bottle containing water and cotton boll with undried fiber, as used in pure-culture incubation with microorganisms to test for the production of fluorescent fiber. Details on p. 1009.

Each of the three fungi found commonly on greenish-yellow fluorescent spots in commercial cotton was tested for its ability to produce fluorescence in the laboratory incubation test. Tests of six isolates of *A. flavus* from natural BGY spots (Footnote 2, Table II) disclosed that the growth of all isolates resulted in a bright greenish-yellow fluorescence on the undried fiber of at least some of the incubated bolls and that some isolates effected fluorescence on the fiber of all bolls. In addition, a similar fluorescence resulted from the growth on the fiber of the key culture *A. flavus* NRRL No. 482 [13, p. 263]. Seven *A. niger* isolates from natural BGY spots were tested in the same manner; in no case did fluorescence result. In addition, the fiber which had been incubated with *A. niger* differed from that in natural BGY spots by having a low aqueous-extract *p*H, averaging around *p*H 4.0, whereas fiber from the natural BGY spots and from *A. flavus*-incubated locks averaged about *p*H 6.6 and 6.3 respectively. Growth of *Rhizopus* isolates resulted in a fluorescent material but apparently only in the aerial mycelium of the fungus rather than in the cotton fiber; the color of this fluorescence was somewhat bluish, rather than bright greenish-yellow. Incubation of *A. flavus* No. 482 on fluffed cotton fiber in a water-vapor-saturated atmosphere by the method previously described [8] promptly resulted in a fiber with a *p*H of 9.5–10.0, with no accompanying change in fluorescence. Any effect of *A. flavus* in bringing about fluorescence in nature must necessarily take place, therefore, on undried fiber.

The ability of *A. flavus* to cause strength loss along with fluorescence was established in an experiment in which Pressley strength determinations were made on locks from 4 bolls incubated with the fungus for 14 days in comparison with values on similarly incubated but sterile control samples. The former yielded Pressley values (1-mm gap jaws) of 2.58, 3.04, 2.76, and 3.29, in comparison with 4.90, 4.98, 4.34, and 4.66 for the latter, each figure being an average from 5 breaks.

Chromatography of Extracts from Natural BGY Fiber and from Fiber Incubated with Fungi

Chromatographic analysis demonstrated a strong similarity of behavior between the fluorescent substance from natural BGY fiber and that in fiber incubated with *Aspergillus flavus*. It was noted that the fluorescent material of natural BGY fluorescent fiber was readily extractable in water and that upon being chromatographed in an isopropyl alcohol-water-acetic acid system extracts from samples from many different locations of growth each gave a single prominent fluorescent spot and that the R_f values obtained for the different samples were identical

within the limits of error of the method. Further, chromatography of an extract from *A. flavus*-incubated fiber resulted in R_f values identical with the values obtained for extracts from field samples. Fiber incubated with different *A. flavus* isolates yielded in all cases identical R_f values. Data on the above points is to be seen in Table II. Paper chromatography was carried out in an ascending system, using a solvent containing 125 parts of isopropyl alcohol, 70 parts distilled water, and 5 parts glacial acetic acid by volume. The BGY fluorescent substance was extracted from 2–7 mg of fluorescent fiber with 1–2 drops of water. This solution was then spotted directly onto the paper. After the spots were dry, the paper was rolled into a cylinder, clipped, suspended over the solvent for 2 hr at 20°C, and then lowered into the solvent. After 16 hr at 20°C, the paper was removed and dried at room temperature and the R_f values were read under ultraviolet light.

As is frequently the case in chromatography, some fluctuation in R_f values occurred from one experiment to the next (Table II), but this fluctuation was not regarded as serious, comparisons always being made within the data of an individual experiment. When an extract from a fluorescent sample from the field (Blythe) was mixed with an extract from *A. flavus*-incubated fiber and the mixture chromatographed, no separation occurred, only a single fluorescent spot appearing on the paper. When the same paper was unrolled, dried, rerolled in the opposite direction, and the spot chromatographed at a 90° angle to its first movement, it still remained without separation as a single spot.

Good agreement of R_f values was also obtained when extracts from field and *A. flavus*-incubated samples were chromatographed with other solvent systems. Thus, in a system with 30 parts isopropyl alcohol, 68 parts water, and 2 parts concentrated ammonia, an extract from the Blythe sample yielded a single spot with an R_f of 0.68, as compared with 0.69 for an extract from fiber incubated with *A.*

TABLE II. R_f Values for Fluorescent Material in Aqueous Extracts from Bright Greenish-Yellow Fluorescent Fiber from Several Classers' and other Samples for Comparison with each Other and with R_f Values for Fluorescent Material in Aqueous Extracts from *Aspergillus flavus* Incubated Fiber

(Close agreement of values within each experiment is considered to support the belief that *A. flavus* is the cause of bright greenish-yellow fluorescent spots in commercial cotton.)

Source of Extracted Fiber	R_f
Experiment #1	
Birmingham, Ala.	0.53
Roll, Ariz.	0.52,* 0.54, 0.53, 0.54, 0.54, 0.54, 0.54
Blytheville, Ark.	0.52, 0.52
Little Rock, Ark.	0.52
Blythe, Calif.	0.52
El Centro, Calif.	0.52, 0.52, 0.52, 0.52, 0.53, 0.52
Raleigh, N. C.	0.51
Austin, Tex.	0.54, 0.54
Corpus Christi, Tex.	0.52, 0.51, 0.53, 0.52, 0.53, 0.52, 0.52, 0.52, 0.53, 0.52
A. flavus incubation (isolate #153)	0.52
Experiment #2	
Hayti, Mo.	0.51
Austin, Tex.	0.52, 0.51, 0.50, 0.50*
Corpus Christi, Tex.	0.51, 0.51, 0.52, 0.52, 0.52, 0.52, 0.52, 0.52
Harlingen, Tex.	0.51, 0.51
A. flavus incubation (isolate #153)	0.51

Source of Extracted Fiber	R_f
Experiment #3	
Sample from D. Nickerson, unknown origin	0.49
Sample from K. T. Louis, grown in Ariz.	0.51
Sample from K. T. Louis, unknown origin	0.49
Sample from J. P. Elting, grown in Ariz.	0.48
Sample from O. Niles, grown in Calif.	0.49
Sample from S. Evans, Blythe, Calif.	0.50
A. flavus incubation (isolate #144)	0.48
Experiment #4	
Blythe, Calif. (1953 crop)	0.43, 0.43, 0.43
O. Niles (grown in Calif. in 1953)	0.43, 0.42, 0.43
Yuma, Ariz. (1954 crop, bale 257)	0.44
Yuma, Ariz. (1954 crop, bale 258)	0.44
Yuma, Ariz. (1954 crop, bale 262)	0.43
Coachella, Calif. (1954 crop, bale 282)	0.42
A. flavus incubation (isolate #144)†	0.43
A. flavus incubation (isolate #153)	0.45
A. flavus incubation (isolate #154)	0.43
A. flavus incubation (isolate #164)	0.42
A. flavus incubation (isolate #165)	0.42
A. flavus incubation (isolate #166)	0.43

* Each figure represents an R_f on an extract from a separate classers' bale sample, not a separate figure for each of several fluorescent spots in a single sample.

† Source of fiber from which isolations were made: #144 and 153, Blythe, Calif.; #154, San Benito, Tex.; #164, Charleston, Mo.; #165, Austin, Tex.; #166, Dallas, Tex.

flavus #153. In a system with 40 parts butanol, 10 parts glacial acetic acid, and 50 parts water, the Blythe sample yielded a single spot with an R_f of 0.18, as against 0.17 for an extract from laboratory-incubated fiber. With 5% Na_2HPO_4, both extracts resulted in a single spot with an R_f of 0.51.

When the fluorescent material from *Rhizopus*-incubated bolls was chromatographed, three different fluorescent spots were obtained from each extract, two of the spots being of such an R_f as to be distinctly different from any spot ever observed with natural BGY material. *Rhizopus* is notorious for the extreme rapidity of its growth; its repeated detection in the mycological examination of natural BGY fiber probably indicated merely that spores of the fungus were often present on the fiber. *Rhizopus* boll rot, which is very common in western cotton, may well have been present in the fields from which BGY fiber was obtained. The same may also have been true of *A. niger;* these two fungi cause two of the most common boll rots of western cotton.

Absorption Spectra of Fluorescent Material from Field and A. Flavus-Incubated Fiber

Absorption spectra were determined in order to supplement data yielded by paper chromatography on the similarity of the fluorescent material in field and *A. flavus*-incubated samples. Two grams of fluorescent fiber from the Blythe sample was extracted at room temperature with distilled water until no fluorescence was observable in the fiber. Isopropyl alcohol was then added to the extract so as to give a solution of 90% isopropyl alcohol. The solution was allowed to stand overnight at 10°C and then was filtered cold through a fritted glass filter (*F*), and the dark orange precipitate discarded. The filtered solution was then added to a prepared powdered cellulose column (12 in. × 1 in.) which had been previously washed thoroughly with 90% isopropyl alcohol and chromatographed, using suction, at a rate of about 30 ml per hr. The column was first eluted with 90% isopropyl alcohol, to effect maximum separation of the bands, until the lowest band had travelled about one half of the distance down the column. Then 85% isopropyl alcohol was used to elute the substances from the column. Fluorescent fiber from bolls inoculated with *A. flavus* was treated in the same manner, using a freshly prepared column.

During chromatography, both samples exhibited fluorescent bands in addition to that recognizable as BGY, but these other bands were much less prominent than the BGY band. The *A. flavus* column had a total of at least 5 definite bands, while the Blythe column had only 3. Only the collected fraction (15–20 ml) comprised of the central portion of the BGY band of each column was prepared for the determination of the absorption spectra. A portion of each of these two fractions was evaporated at 30°C under vacuum. The resultant residues, with no further attempt at purification, were readily and completely taken up in Pyrex glass-distilled water. Appropriately diluted, solutions were made up so as to contain: (a) 0.1 *N* HCl; (b) 0.4 *N* NaOH; and (c) 0.1 *M* PO_4, *p*H 7.0. Absorption spectra (Figure 2) of these solutions were then determined at 2-mμ intervals with a Beckman DU spectrophotometer. Care was taken not to expose these substances to strong light, all of the operations prior to spectrophotometry being carried out in a very dim light or darkness.

Though the absorption spectra are not identical, as is indicated by the disparity in the absorption peak ratios, it is apparent that the two partially purified substances do resemble each other very closely. Of further evidence for this similarity is the marked parallel of shifts in absorption at the different *p*H levels. Both of the fractions chromatographed on paper yielded R_f values identical to that of the Blythe sample, which was used as a standard throughout the paper chromatography work.

Previous microbiological assays [1], employing *Lactobacillus casei,* had demonstrated that aqueous extracts of both natural BGY fiber and *A. flavus*-incubated fluorescent fiber failed to exhibit riboflavin activity. The absorption spectra presented in Figure 2 also preclude the possibility of BGY being riboflavin. This point was of interest because Pontovich [9] has reported data which indicated the production of riboflavin by *A. flavus* on a synthetic medium.

Other characteristics of the fluorescent BGY substance are: (1) a positive test with ferric chloride, giving a brownish (amber) color diagnostic for the presence of phenolic groups, and (2) a negative test upon heating with magnesium and concentrated hydrochloric acid. Certain flavins and other compounds yield a purple color when reduced in the latter test.

For both BGY spots and *A. flavus*-incubated fiber, fluorescence was materially decreased by ex-

posure of the fiber to sunlight for 2 days, as was also the yellow color visible in daylight.

Geographical Areas of Origin of Fiber Containing BGY-Fluorescent Spots

To date, high percentages of samples containing BGY spots have been found from only two areas of U. S. production, namely, from the general region of Yuma, Arizona (including a nearby area in California around Blythe) and from the Brownsville-Harlingen area of Texas. Lower percentages of samples with BGY-fluorescent spots were noted from various other regions of Texas and very occasional samples with the same type spots from essentially all of the other U. S. producing areas. The number of spots per sample was lower for areas other than the Yuma and Brownsville areas. The above general conclusions are made on the basis of examination under ultraviolet light of about 2000 classers' samples from the 1954 crop of all major U. S. cotton-growing regions, these samples having been selected at random from an extensive grade survey series made available to us through the helpful courtesy of Miss Dorothy Nickerson of the U.S.D.A. Agricultural Marketing Service.

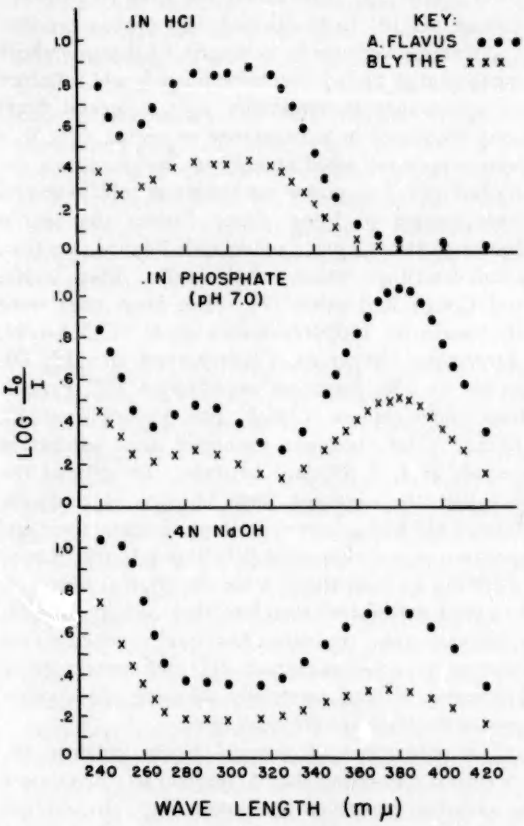

Fig. 2. Absorption spectra of partially purified fluorescent material from naturally fluorescent fiber (Blythe, Calif.) and from *A. flavus*-incubated fiber, both at three conditions of *p*H. (See text, p. 1012.) Data considered to supplement the evidence from mycological observations and data of Table II in supporting belief that *A. flavus* is the cause of bright greenish-yellow fluorescent spots produced in cotton under field conditions.

There is no evidence known to the writers to support a belief that the occurrence of BGY spots in cotton is a new development in the United States, even though its cause is here identified for the first time, nor that it is more prevalent now than formerly. A classer of long experience states that yellowish spots have been found in Arizona cotton for many years [12]. It may be noted that the Brownsville area is one in which the pink bollworm is prevalent; it would not seem unreasonable to suspect that *A. flavus* may gain entry to bolls in some instances by way of injuries caused by this insect, but no critical evidence on the point is known to the writers. The pink bollworm was believed to have been absent from the Yuma area in 1954. Since *A. flavus* occurs as a common inhabitant of soils in numerous cotton-growing areas other than around Yuma and Brownsville, one may wonder why the BGY spotting is so common in the latter areas and less common elsewhere. No answer to this question is known to the writers at the present time.

Spots with a White Fluorescence, Associated with the Fungus *Alternaria* Sp.

The only type of fluorescent spot in raw cotton other than the BGY spot which has been found frequently and determined to be of microbial origin is a white spot associated with *Alternaria* sp. White spots are quite common in cotton from a wide variety of locations. Data in Table III present results of the chromatographic analysis of extracts from fluorescent spots in field samples in parallel with extracts from the fiber of bolls which had been incubated in pure culture with various *Alternaria* isolates. The fiber was extracted with 70% acetone and then with pure acetone and the combined extract chromatographed as with BGY extracts, except that the solvent contained 70 parts isopropyl alcohol, 125 parts water,

and 5 parts concentrated ammonia. Although there was a variation in the general level of R_f values in the two experiments of Table III, it may be seen that within each experiment the values for the three fluorescent spots from the incubated-fiber extracts matched closely the values for the extracts from the field samples. It should be noted that no claim is made to the effect that *all Alternaria* isolates produce these fluorescent spots, this capability being more probably restricted to particular strains of *Alternaria*.

Types of Fiber Samples Which Failed to Show Distinctive Fluorescence

During the past several years, numerous sporadic observations have been made on cotton under ultraviolet light at Beltsville: on weathered vs unweathered fiber, on fiber inoculated with various microorganisms and incubated, and on various other types of special or unusual cotton fiber. With the exception of confirmation in a general way of the effect of ageing and heat on fluorescence [10] and of observations on certain samples stated to be contaminated with "tramper grease," the results were essentially negative in the sense that no striking differences in fluorescence were observed. Cotton which had turned grayish during 10-wk weathering prior to harvest looked somewhat duller under the lamp than unweathered fiber, but the difference in appearance was not striking, certainly not more so than in daylight. This weathered fiber was known from microscopic observation and from its aqueous-extract *p*H [8] to be infested with microorganisms.

Attempts were made to determine if pure-culture incubation of fluffed fiber with fungi would influence its appearance in ultraviolet light. Several fungi were incubated in pure culture on cotton fiber in a water-vapor-saturated atmosphere, as previously described [7], i.e., under conditions in which several were known to bring about distinct changes in aqueous-extract *p*H, reducing-substance content, alkali-centrifuge value, alkali-swollen fiber width, and Congo Red value [7]. The fungi used were *Alternaria* sp. 140, *Aspergillus niger* TC-215-4247, *Aspergillus terreus* 45, *Cladosporium* sp. 113, *Diplodia* sp. 136, *Fusarium moniliforme* 102, *Penicillium ochro-chloron* 1336.2, and *Stemphylium* sp. 1203.1. The fiber was examined after incubation periods of 4, 7, 11, and 14 days. In spite of the fact that the expected large changes in aqueous-extract *p*H had occurred in these samples, their appearance under ultraviolet light showed little, if any, alteration in comparison with the original fiber. It has been established therefore that certain common fungi may grow on cotton fiber and produce major changes in aqueous-extract *p*H and certain other properties without materially affecting the appearance of the fiber in ultraviolet light.

The occurrence of unusual fluorescence is apparently a rare rather than a common accompaniment of microbial growth on raw cotton fiber. In addition to the above types of samples, failure to observe any unusual or characteristic fluorescence was also found for the following types of fiber: fiber naturally infested with either *Diplodia* sp. or *Collectotrichum* sp. in the tight-lock condition, fiber infested with *Aerobacter cloacae* [4], fiber infested with the bacterial blight organism *Xanthomonas malvacearum*,

TABLE III. R_f Values for Fluorescent Materials in Extracts from Whitish-Fluorescent Fiber from Several Classers' Samples for Comparison with Each Other and with R_f Values for Fluorescent Materials from Fiber Incubated with *Alternaria*

Source of Extracted Fiber*	R_f Values†
Experiment #1	
Leachville, Ark.	0.46, —, 0.67
Rector, Ark.	0.48, 0.56, 0.66
Raleigh, N. C.	0.46, —, 0.66
Oklahoma City, Okla., Sample #1	0.46, 0.56, 0.66
Oklahoma City, Okla., Sample #2	0.46, 0.56, 0.65
Jackson, Tenn.	0.44, —, 0.64
Corpus Christi, Tex., Sample #1	0.47, 0.57, 0.67
Corpus Christi, Tex., Sample #2	0.46, —, 0.66
Corpus Christi, Tex., Sample #3	0.47, 0.56, 0.67
El Paso, Tex., Sample #1	0.47, —, 0.67
El Paso, Tex., Sample #2	0.48, —, 0.67
Alternaria-155 Incubation #1	0.45, 0.53, 0.64
Alternaria-155 Incubation #2	0.47, 0.56, 0.67
Alternaria-155 Incubation #3	0.45, 0.53, 0.64
Experiment #2	
Classers' Sample, Altus, Okla.	0.35, 0.56, 0.63
Classers' Sample, New Madrid, Mo.	0.36, 0.57, 0.64
Classers' Sample, Oklahoma City, Okla.	0.36, 0.56, 0.64
Classers' Sample, Corpus Christi, Tex.	0.36, 0.56, 0.64
Incubated Fiber, Alternaria #148	0.35, 0.54, 0.61
Incubated Fiber, Alternaria #151	0.36, 0.56, 0.62
Incubated Fiber, Alternaria #152	0.34, 0.55, 0.62
Incubated Fiber, Alternaria #155	0.35, 0.56, 0.63
Incubated Fiber, Alternaria #169	0.35, 0.56, 0.63
Incubated Fiber, Alternaria #170	0.35, 0.57, 0.64
Incubated Fiber, Alternaria #173	0.36, 0.57, 0.64
Incubated Fiber, Alternaria #176	0.36, 0.56, 0.64

* In all of the classers' samples listed, fluorescent strands of fiber from the same sample had been incubated on water agar and had developed a moderate to very heavy growth of *Alternaria* sp. In most cases there was little or no growth of other fungi.

† Each set of 2 or 3 values corresponding to a sample entry indicates the number of discrete spots appearing after chromatography of a single extracted sample.

fiber with a deposit of aphid honey dew and with attendant microbial growth, thin-walled fiber from potassium-deficient plants, tinged cotton, and green-lint or high-wax cotton. In the writers' experience, honey dew on cotton is found as a dark crusty deposit eventually consisting almost entirely of the mycelia of dark-walled fungi, especially *Cladosporium;* it shows little if any fluorescence under the conditions of observation here employed. In addition, various defoliating chemicals which are commonly used on cotton plants and which may contaminate the fiber also exhibited little or no fluorescence; the compounds tested included calcium cyanamide, sodium cyanamide, sodium chlorate, potassium ethyl xanthate, endothal acid monohydrate, potassium cyanate, and pentachlorophenol, all in the form of pure chemicals at a concentration of 1% on cotton fiber. Several samples obtained from Dr. Burt Johnson which were stated to be contaminated with "tramper grease" contained very large oily spots which exhibited a pronounced yellow fluorescence. They were clearly to be differentiated from BGY spots, on the basis of their greater size (several grams of fiber), obvious contamination with oil, and markedly less brilliant fluorescence.

Discussion

Some isolates of *A. flavus* failed to produce visible fluorescence on every inoculated and incubated boll. Within a single group of bolls, all inoculated at the same time and incubated under apparently identical conditions, some bolls showed bright or very bright fluorescence, while others with an equal or possibly greater amount of growth showed little or none. This behavior was characteristic of isolate 144, obtained from the Blythe sample. A common cause of variability in "pure culture" experiments is the presence of a contaminating organism. However, isolate 144 was carefully checked and found pure, and careful examination of nonfluorescent incubated locks revealed the presence of no foreign organism. Incubation of fiber with isolate 153, also from the Blythe sample, resulted, on the other hand, in a high degree of fluorescence on all bolls in all of the numerous inoculations made with it on intact undried fiber.

It was considered as a possibility that the production of fluorescence might in some way entail infection of the seed. However, small tufts of undried fiber cut away from the seed and incubated with *A. flavus* 153 on the surface of water agar developed a pronounced and typical BGY fluorescence. The cutting of the fiber cells may be assumed to have "killed" them, although it is not certain that still-active fiber enzymes may not have participated with the fungus in the formation of the fluorescent compound. Attempts to obtain fluorescence by incubation of *A. flavus* on undried fiber which had been previously frozen or autoclaved were unsuccessful.

Inasmuch as incubation of a detached boll in a fruit jar as described here represents an artificial type of procedure, a question was raised as to whether *A. flavus* would cause fluorescence when inoculated into a cracked boll on the plant in the greenhouse. This experiment was successful in the sense that the typical fluorescence was produced. It was necessary to maintain a high humidity around the boll by enclosing it in a cellophane bag, an experimental procedure, it may be noted, which is reminiscent of the environmental conditions described for the plants from which the Blythe sample was collected.

The practical importance of fluorescent spots in cotton is difficult to assess at the present time. One individual with extensive experience in "trouble-shooting" for cotton mills states that the occurrence of bright greenish-yellow fluorescent spots in the fiber is associated with serious difficulties in spinning [2]. A firm which markets ultraviolet lamps for use in the examination of raw cotton and cotton products refers to certain fluorescent-spotted cotton as "cat-eye" cotton and claims that such cotton causes difficulties in dyeing. A typical sample of ginned lint with a natural infection of *A. flavus* was sent to this firm and after examination by them was stated to be identical with "cat-eye" cotton [5]. Since BGY spots are easily recognizable, interested spinners and others concerned with cotton could identify them and determine for themselves the extent to which they may interfere in their operations. Individuals using or contemplating the use of ultraviolet lamps should be informed in respect to the possible health hazards to operators and the necessary precautions to be taken. The fluorescent spots here described are readily visible under a 3660-peak lamp as well as under the type here used, and the former may be more desirable from a safety standpoint.

The "old ivory" fluorescent color found by Sheehan, Bailey, and Compton [10] to result from either heat or age does not resemble either *A. flavus* or *Alternaria* spots in any way. The only other reference to fluorescence in cotton known to the writers is the "brown line" phenomenon of Bogaty, Campbell, and Appel [3]. This phenomenon has been reported in textiles but not in raw cotton; if it occurs

in raw cotton there seems little likelihood that the appearance produced could be confused with that of the fluorescent spots here described.

Acknowledgment

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Note on the Lignin and Hemicellulose of Jute

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Abstract

Some facts about a combination between lignin and polyuronide hemicellulose of jute fiber are noted. An alkali lignin has been isolated from the fiber and described. An approximate estimate has been made of the different constituents removed by dilute caustic soda at ordinary temperature from jute.

Introduction

In recent years, many investigators have studied jute fiber and a number of interesting facts have come to light [13, 14]. The chemistry of the fiber is, however, still obscure, and a lot remains to be known. Facts collected in these laboratories during the last decade and a half have mostly been published [15]. In the present communication are reported some facts relating to the existence of a combination between hemicellulose and a portion of the lignin, alkali lignin, and some of its properties and the easy removal of lignin after a mild alkali treatment.

Experimental

Lignin-Polyuronide Hemicelluloses Linkage in Jute Fiber

Based on the rates of delignification of defatted jute before and after treatment with dilute caustic soda at room temperature and the rise in acid value after such alkali treatment, as well as with the progressive removal of lignin, a hypothesis on the combination between lignin and the uronic acid part of the hemicellulose was put forth [16]. This has recently been corroborated by Bhattacherjee and Callow [1]. Further evidence now available supports this view.

In the method for the estimation of cellulose in defatted jute using 0.7% sodium chlorite at *p*H 3–4 on boiling water bath (fiber: liquor ratio 1:50) for 2 hr, it was claimed that, under the conditions specified, lignin was more or less completely removed from the fiber [4]. Subsequent work has, however, shown that a little lignin, as a chloro-derivative, is tenaciously retained by the holocellulose which gives the characteristic pink color with chlorine water and sodium sulfite solution. This chloro-compound may be extracted from the holocellulose with very dilute caustic soda solution at ordinary temperature and obtained as a light-yellow powder by boiling the extract with excess of dilute mineral acid, which hydrolyzes the polysaccharides to water-soluble products. The analytical data for the chloro-compound are given in Table I. Furfural was determined by the phloroglucinol method according to the procedure of A. W. Schorger [10]. Carbon dioxide was determined by distilling the material with 12% HCl and absorbing the gas in gas-washing bottles containing decinormal baryta solution [11]. By distilling the material with 28% H_2SO_4, formaldehyde was obtained in the distillate, which was estimated with dimedone. Methoxy value was determined by a semimicro method, distilling with HI and phenol, absorbing the CH_3I in glacial acetic acid solution of potassium acetate and bromine, and titrating with decinormal thiosulfate. Chlorine was estimated with calcium oxide and sodium carbonate, following the method of Piria and Schiff [5]. The chloro-compound of lignin has 18.56% methoxyl and 9.49% chlorine. It gives no furfural and reduces Fehling's solution, but no simple sugar could be detected by paper partition chromatography in the hydrolysate. This might be due to partial loss of dioxymethylene group and liberation of two phenolic hydroxyl groups during treatment with sodium chlorite (cf. figures for formaldehyde in Tables I and VI). On treatment with 72% sulfuric acid, as in lignin determination, about 75% of the chloro-compound could be recovered.

While bleaching jute with chlorite, it has been noticed that a very mild alkaline pretreatment largely facilitates delignification and a milk-white fiber thus results. Estimation of "lignin" in the chlorite holocellulose obtained from defatted jute before and after a mild alkali (1%) treatment shows the effect of such pretreatment. The figure for "lignin" falls to 0.17% in the latter case (see Table II). A mild alkali pretreatment thus appears to be essential for the *complete* removal of residual lignin from jute fiber. A 0.5% caustic soda treatment at ordinary temperature for half an hour is almost equally effective. Caustic soda seems to hydrolyze the ester linkage between lignin and uronic acid of hemicellulose, which is apparently resistant to the action of sodium chlorite; only a portion of the lignin in jute is thus combined. This view is supported by the methoxy values of defatted jute before and after alkali treatment and of the corresponding holocelluloses isolated therefrom. Thus while defatted jute before and after 1% caustic soda treatment has 4.24 and 4.06% methoxy, respectively, the holocelluloses obtained from them have 1.52 and 0.44% methoxy, respectively (see Table III).

The slight fall in methoxy value of defatted jute on treatment with 1% caustic soda is mainly due to the removal of alkali-soluble lignin (see above). The appreciable difference between the methoxy values of chlorite holocellulose obtained from defatted

TABLE I. Analysis of Chloro-Compound Isolated from Chlorite Holocellulose

	Per Cent
Methoxy value	18.56
Ash	0.85
Furfural	nil
Chlorine	9.49
Formaldehyde	0.91
Carbon dioxide	1.19

TABLE II. Per Cent "Lignin" in the Chlorite Holocellulose

From	J3435 (White)	J3519 (Tossa)
Defatted jute	2.80	2.44
Do pretreated with 1% caustic soda for 1 hr at room temperature (fiber:liquor ratio 1:30)	0.17	0.17

TABLE III. Methoxy Values of Jute, Raw and Treated, and of Holocelluloses Therefrom

Experiment No.	Material	Methoxy Value (%)
1	Raw jute (J.KMD)	4.25
2	Do defatted with alcohol-benzene	4.24
3	Defatted jute treated at room temperature with 1% caustic soda for 2 hr (fiber:liquor ratio 1:50)	4.06
4	Chlorite holocellulose from (2)	1.52
5	Chlorite holocellulose from (3)	0.44
6	Chlorite holocellulose from defatted jute treated with 0.5% caustic soda for ½ hr at room temperature (fiber:liquor ratio 1:50)	0.60

TABLE IV. Yield of Alkali-Lignin from Jute at Room Temperature

Sample	Strength of NaOH (W/V) (%)	Alkali-Lignin (%)	Residual Lignin in the Fiber (%)	Total Lignin (%)
J3512 (*caps.*)	nil	—	—	12.00
Do treated with NaOH	1	0.44	11.93	12.37
Do treated with NaOH	5	0.50	11.32	11.82
Do treated with NaOH	10	0.66	11.60	12.26
J3910 (*olit.*)	nil	—	—	13.24
Do treated with NaOH	1	0.30	12.90	13.20
Do treated with NaOH	5	0.43	12.53	12.96
Do treated with NaOH	10	0.52	12.50	13.02

jute before and after alkali treatment (experiments 4 and 5 in Table III) may be explained on the assumption that the alkali sets free, by hydrolysis, the combined lignin, which is then dissolved by sodium chlorite (see Table II). While the chlorite holocellulose from defatted jute gradually turns yellow and becomes dull on storage rather rapidly, that from alkali-pretreated fiber maintains its white color and gloss for quite a long time. The wet strength of such fiber is, however, very low compared with that of ordinary delignified jute.

Alkali-Lignin from Jute Fiber

Isolation of lignin from lignified materials by means of alkali and its characterization have been ably reviewed by Brauns [3]. That dilute caustic soda at room temperature may remove a portion of the lignin in jute fiber has been suspected but no alkali-lignin seems to have been isolated. The percentage figures for residual lignin in defatted jute, before and after treatment with caustic soda solution of varying strength at ordinary temperature, determined some years ago and expressed on defatted jute, agreed fairly closely. Attributing the small difference to the usual experimental error, it was concluded that caustic soda solution, up to 20%, did not materially affect the lignin of jute fiber [17]. On a closer examination, it has been found that a dilute solution of caustic soda at room temperature removes a small portion of the lignin from jute. Thus, by extracting the defatted fiber with 1% caustic soda solution at room temperature for about 2 hr, a brown solution is obtained from which a pale yellow flocculent precipitate separates after acidification with hydrochloric acid. This becomes granular on heating the liquid to boiling. Extracts with stronger solutions of the alkali turn turbid on acidification (no immediate precipitation occurs) and give a granular precipitate on boiling. Analytical data of this compound indicate that it is lignin (see Table VI). The yield of alkali lignin from one sample of *capsularis* and one of *olitorius* jute fiber, following the above procedure, is shown in Table IV. Lignin was determined with 72% sulfuric acid after 5% sulfuric acid treatment on a boiling water bath.

It seems likely that a portion of the alkali-lignin remains dissolved in the acid filtrate (which is colored) inasmuch as water appears to dissolve a little of the lignin from the fiber. Furthermore, the amount of residual "lignin" in chlorite holocellulose prepared from defatted jute without alkali pretreatment is about 2.5%.

The amount of jute lignin, soluble in caustic soda at ordinary temperature and precipitated by acid, is thus small and falls almost within the limits of experimental error in lignin determinations. That is why it has escaped notice so long. The percentage yield of alkali lignin does not increase appreciably on repeated extraction of the fiber (see Table V). Jute thus behaves somewhat differently from straw [2].

Alkali-lignin from jute is a yellowish gray, odorless, amorphous powder, readily soluble in pyridine or phenol, moderately soluble in dioxan, slightly

TABLE V. Per Cent Yield of Alkali-Lignin on Repeated Extraction

Room temperature, 32°C. Fiber:liquor ratio 1:25. Time, 2 hr for each treatment. Strength of NaOH solution 10% (W/V).

Sample	No. of Extractions	Alkali Lignin (total) (%)
J3512 (defatted)	1	0.66
J3512 (defatted)	4	0.70
J3910 (defatted)	1	0.52
J3910 (defatted)	4	0.58

TABLE VI. Analytical Data for Alkali-Lignin from Jute

	Per Cent
Methoxyl value	19.25
Ash	0.43
Furfural	nil
Loss on treatment with 72% H_2SO_4 as in lignin determination	12.37
Residue left on treatment with Textone (sodium chlorite) at *p*H 5 on boiling water bath for 2 hr	1.0
Ethanol-insoluble residue after exhaustive chlorination in carbon tetrachloride suspension	3.70
Yield of formaldehyde on distilling with dilute sulfuric acid	2.8
Molecular weight (cryoscopic method) in dioxan	3370
in phenol	3520

soluble in glacial acetic acid, acetone, and methanol, and practically insoluble in ether, chloroform, glycol, and ethanol. It does not reduce Fehling's solution and gives a pink color with chlorine water and sodium sulfite solution but remains colorless with phloroglucinol in hydrochloric acid. No simple sugar could be detected in the acid hydrolysate of alkali-lignin by means of paper partition chromatography. Alkali-lignin is not hygroscopic.

Action of Dilute Caustic Soda on Jute Fiber

In wet processing of jute, e.g., alkaline bleaching, jute comes in contact with dilute alkaline solution. It is worth while to know what constituents of the fiber are thus removed and to what extent. As jute fiber contains some fat and wax, a fairly large proportion of which is unsaponifiable (it also contains varying amounts of chlorophyll), fiber thoroughly extracted with alcohol-benzene (1:1) is used in these experiments. Loss in weight, which a clean defatted fiber suffers on treatment at room temperature with caustic soda solution of varying strength, has been reported [17]. The action of 1% caustic soda on the different constituents of the fiber is mainly detailed here. The analytical data of the two varieties of jute used, one *capsularis* and one *olitorius*, are given in Table VII.

Acetyl groups in jute fiber, detected long ago, are probably linked with the carbohydrate portion [18]. Dilute caustic soda at room temperature removes these groups almost completely. Loss of acetyl accounts for about half the weight loss on alkali treatment. This has also been observed by Macmillan and Sen Gupta [12]. As already stated, a little lignin is removed during extraction with dilute caustic soda at room temperature. The actual figure is presumably higher than that of alkali-lignin, which is not completely precipitated by acid. The third constituent removed is the hemicellulose. Though in the hydrolyzate of the boiling water extract of defatted jute, arabinose, xylose, galactose, and possibly mannose were detected by paper partition chromatography, it has been possible to detect only xylose, arabinose, and galactose in the hydrolyzate of dilute caustic soda extract. As alkali-lignin is nonreducing and the alkaline extract of jute fiber after boiling with dilute mineral acid reduces Fehling's solution, reducing sugars are estimated as usual and calculated as xylose. Some of the mineral constituents are also removed by the alkali, as indicated by the fall in ash content of the alkali-treated fiber. Silica, for example, mostly goes into the alkaline extract. Some nitrogenous matter also dissolves in the alkali (see Table VIII).

Only a little of the hemicelluloses dissolves in 1% caustic soda. The furfural figures for the defatted fiber (J3910), before and after alkali treatment, viz., 9.86 and 9.44% (both calculated on defatted jute), show that little xylan-methyluronic-acid complex disappears during such treatment. Some coloring matter also may dissolve in the alkali. The figures in Table VIII are approximate inasmuch as it is hardly possible to account for and adjust the change in weight due to addition of water on hydrolysis; the

TABLE VII. Analytical Data for Defatted Jute Fiber

	J3910 (*olit.*)	J3512 (*caps.*)
Chlorite holocellulose	88.61	88.98
Alpha-cellulose	62.09	62.47
Furfural	9.86	8.51
Carbon dioxide	1.46	1.37
Ash	0.89	0.77
Lignin	13.24	12.00
Acetyl (CH_3CO—)	3.62	3.95
Nitrogenous matter (% $N_2 \times 6.25$)	1.00	1.00

TABLE VIII. Per Cent Loss of Constituents of Defatted Jute Fiber on 1% NaOH Treatment at Room Temperature

	J3512	J3910
Acetyl (CH_3CO—) groups	3.6	3.3
Reducing sugar (as xylose)	1.08	0.82
Alkali-lignin	0.44	0.30
Ash	0.55	0.58
Nitrogenous matter (% $N_2 \times 6.25$)	0.26	0.25
	5.93	5.25
Per cent extracted by 1% NaOH	7.5	5.3

All figures are expressed on 100 g of bone-dry material.

amount of lignin remaining in solution on acidification of alkaline extract could not be determined.

Discussion

With 10% (W/V) caustic soda at room temperature, the defatted fiber suffers a much greater loss (15.1% for J3512 and 11.4% for J3910, compared with 7.5% for J3512 and 5.3% for J3910 with 1% caustic soda); this is largely due to the removal of hemicelluloses (as shown by the analytical data of the treated fiber); the residual lignin in the fiber, however, remains practically unaffected, and the amount of lignin dissolved in the alkali and precipitated by acid is practically the same. Simultaneous fall of furfural and uronic carbon dioxide values for jute treated with 10% caustic soda supports this view.

The light, yellowish-gray alkali lignin becomes deep brown with alkali and returns to its original color on acidification. As is well known, jute fiber turns brown with alkali; also, it gives a lighter shade with very dilute mineral acids. The alkali lignin *in situ* may partly contribute to such changes in color.

That dilute caustic soda solution in the cold breaks the lignin-polyuronide hemicellulose bond in jute fiber appears to be certain. Complete delignification without alkali treatment seems to be impossible. The ease of removal of lignin in Cross and Bevan's method [7] of cellulose estimation after an alkaline treatment may be readily explained on this basis: Norman and Jenkin's method [8] as well as Schmidt's method [9] involves an alkaline treatment (in the form of hot sodium sulfite); in each case the removal of lignin is complete.

While it is possible to retain about 60% of the wet strength after bleaching ordinary jute with Textone, very little wet strength remains when it is bleached after a pretreatment with 1% caustic soda under otherwise identical conditions. Removal of the combined lignin might be partly responsible for this. Further facts are necessary to explain this big difference. Jute bleached with alkaline hydrogen peroxide to a full white loses only about 3% of lignin [6]; this may represent the combined part. It is, however, difficult to say whether or not the lignin, set free by caustic alkali, dissolves therein as alkali-lignin. A portion of the free lignin may possibly dissolve as alkali-lignin while the combined lignin, set free by the dilute alkali, may be insoluble in it.

Dilute caustic soda extract of defatted jute, on distillation, gives off ammonia; roughly about 10% of the nitrogen in the fiber is thus accounted for. If the nitrogen occurs as protein, this indicates an amido group, $—CONH_2$, therein; alpha-amino-acids give no ammonia on heating with caustic soda.

Acknowledgment

The molecular weight was determined by Dr. P. C. Das Gupta, to whom our thanks are due.

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Manuscript received July 7, 1955.

Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Research Objectives, Methods, and Mentalities

Part I: Productivity in Research[1]

ROHM & HAAS CO.
Philadelphia, Pa.
September 1, 1955

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

With research currently costing nearly four billion dollars a year, contemplation of ways to make it more productive would certainly seem worthwhile.

In the belief that there is room for extended discussion of this very complex subject, the following views are submitted for general consideration—with some reservations, however, for almost any statement on research method is likely to be regarded as highly controversial. This is particularly true if the argument is bluntly stated and not supported by case histories. The present discussion is brief, preliminary, and general, and is presented with the thought that, while fallacies exist in all generalizations, a concise general statement is, nevertheless, the best means of emphasizing an inherent truth.

It seems almost self-evident that the primary goals of research are (1) to gain an understanding of our environment and (2) to learn how to control it. Thus we need scientific knowledge (understanding) and technological know-how (control). Of these, the latter is the ultimate objective insofar as humanity in general is concerned.

Unfortunately, there is a common belief that the basic understanding must come first and the technology later. Thus it is often said that "fundamental research leads the way" or that "we need more basic research to assure a store of new information on which later inventions will be based." It has even been claimed recently that we should have more Ivory Towers, wherein the researcher can carry on his investigations unencumbered by practical considerations.

There are certain fallacies here that are not easily resolved. For it is true that, in many instances, basic research has resulted in new information which was later put to practical use. Yet there are just as many cases where practical applications came long before the basic understanding. Valko [4] cites the example of indigo vat dyeing, where the full scientific explanation was attained 2500 years after the process was developed. Lest it be argued that the textile field is old and underresearched, we might cite photography as a much newer field (about 70 years old) wherein technology has outstripped science, despite considerable basic research [1].

Probably the best progress is made where theory and application evolve side by side, each contributing to the development of the other. This was recognized long ago by Lord Rutherford [3], who said "long term research and ad hoc problems form an indivisible whole." A very recent example is the development of the transistor; Bown [2] states "In this effort we had the traditional motivation and method of scientific research intermingled with the motivation and method of the inventor. The scientist seeks to know and to explain; the inventor is alert to apply. In combination they can create promptly and soundly the new things that their

[1] This is the first of three letters on this subject. Part II will deal with the classification of research and will appear in an early issue. The series will conclude with "The Evolution of Technology." The opinions expressed in these letters are those of the author alone, and do not necessarily reflect the opinions of the author's organization.

work has made possible. The purity and integrity of science are in no sense stultified by the immediacy with which it is translated to human service."

Another important consideration involves the mental processes of the researcher. There is a type of mind that is content with devising and proving theories that explain known facts. (Perhaps the main difficulty with the Ivory Tower, incidentally, is that the rarified atmosphere is conducive to the propagation of this species.) Such an individual may be strong in analytical ability but weak in the ability to associate and integrate ideas in a creative manner. Yet he sometimes disguises this through a clever device: having started with a known fact, worked out an explanation, and garbed it in highly mathematical terms, he presents the mathematics first, deduces the explanation, and predicts the fact. To the uninitiated, it may appear that something has been discovered. Yet well over 75% (unofficial estimate) of all basic research studies merely explain or measure more exactly phenomena which were already clearly recognized, without aiding in any way the prediction of new facts. Such research may have high scientific value, but there is some question as to how productive it is.

In a large organization it is possible to utilize the services of men of both traits—analytical and associative—so that each will supplement the other, to their mutual benefit. Even so, I believe that it will some day be recognized that the most productive men, including the pioneers in every field of science, have been men who were strong in both traits.

Another very unfortunate misconception involves research method. A researcher with a problem to solve cannot afford to be inhibited in his choice of an experimental approach; he cannot always use an "elegant" method. It is unfortunate, therefore, that research methods have too often been classified as either fundamental (and therefore good) or empirical (bad). Actually, there is a spectrum of methods, one shading into the other: (1) trial and error (very empirical); (2) systematic study of variables; (3) working hypothesis; (4) mechanism study (very fundamental).

Trial and error, sometimes regarded as the standby of the poorly educated, has solved many a practical problem. However, it is slow and uncertain. Moreover, the solving of one problem by this method gives little or no insight into the solution of the next. Nowadays such research is frowned on, and rightly so.

At the opposite, most erudite, level are studies of reaction mechanisms, kinetics, steric relationships, and the like. Results may indeed be useful, particularly for extending a discovery that has already been made. But too often the work is carried beyond the point of diminishing returns by a researcher, of analytical frame of mind, who is more interested in merely measuring something, or in proving that a theory is really true, or in obtaining data for a publication than in creating something. Nowadays such research is frequently overrated; its creative value is sometimes a mere illusion, based on clever reporting.

These extreme approaches—trial and error and mechanism studies—might be regarded as high rocky hills whereon the sowing is difficult and the crops are sparse. There is a fertile valley between, which, in the writer's opinion, produces the bulk of our research harvest. On the one side, near the trial-and-error hill, is an area we might call "study of variables." Here the effect of all controllable variables is systematically determined. While it must be regarded as an empirical method (*even in cases where chemical composition is one of the variables*), such an approach is often the best way to begin on a completely unfamiliar problem. Once a few facts have been uncovered, however, the researcher can make faster progress on the other side of the valley, called "working hypothesis." Here he uses his insight to guess at the underlying principles, and—assuming his hypothesis to be true—he uses it to predict the proper steps toward a solution of the problem. So long as it gives him the results he wants, he is not immediately concerned as to whether the hypothesis be true or false. Years later, the fellow in the Ivory Tower on mechanism hill can prove that he was right—or maybe wrong.

Going a step further, a researcher with an associative mind, a good memory, and wide experience can often integrate his new hypothesis with several previously acquired bits of information and come up with some entirely new concepts, or solutions to old problems, or almost anything imaginable. In the opinion of the writer, this is research in its most creative form.

There are no clear-cut dividing lines between the four research methods listed above. We might say, arbitrarily, that the first two are empirical, while the last two are basic or fundamental. But *in the hands of a capable researcher, armed with a fertile imagination, skilled in inductive reasoning and in the setting up of working hypotheses, and fired with ambition to solve a problem, there is usually no distinction between that part of his work which is fundamental and that part which is empirical.*

To show the value of a working hypothesis, we might take as a very homely example the story of Columbus. When it occurred to him that the earth was round, he did not try to set up instruments or invoke higher mathematics to prove that it must be so. Accepting his hypothesis as true, he concluded that he should be able to reach India by going westward. It is this ability to visualize and put to practical use a tentative theory, no matter how nebulous, which distinguishes a creative researcher from one who has his eyes turned toward proving what to his more imaginative fellows has long since appeared fairly obvious.

That Columbus discovered America, instead of reaching India, is quite beside the point; such chance discoveries, often more important than the goal being sought, are an added incentive to the diligent pursuit of an objective. Perkin's synthesis of the first aniline dye while attempting to make quinine is a classic example. Although no study of the subject has been reported, it is likely that most accidental discoveries have been made by those who were following a hypothesis in an attempt to produce practical results, rather than merely trying to confirm it.

This entire problem of research objectives, research methods, and research mentalities is a complex one. It is all too easy to become involved in semantics and to confuse the quest for new facts, even though presently useless (this is one of the objectives of pure research) with what is often called basic research but which refers to a method (such as mechanism studies) for explaining known facts. Actually, pure research can on occasion be empirical, while applied research can sometimes be fundamental. It is important, therefore, that the many adjectives which have been applied to research—such as pure, applied, basic, practical, exploratory, academic, fundamental, empirical, technological—be carefully and logically defined. But this goes beyond the present brief discussion.

My thesis is that (1) sometimes science leads the way and sometimes technology, but the best progress is likely to be made where science and technology evolve side by side, each nurtured by and inspired by the other; (2) the type of mentality which combines associative and analytical traits is likely to be the most creative: and (3) while any research approach can on occasion be productive, the most creative researcher cares little whether his methods are empirical or fundamental and in most cases employs an almost indistinguishable combination of both. Admittedly, however, the subject is a controversial one that deserves much further consideration and discussion.

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A. C. NUESSLE

Textile Education at Massachusetts Institute of Technology

Massachusetts Institute of Technology
Cambridge 39, Massachusetts
October 3, 1955

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

In the July issue of the TEXTILE RESEARCH JOURNAL, Mr. Hayward presents an excellent summary of "Textile Education, Graduate and Undergraduate." It is appreciated that for reasons of time and space he has restricted his comments to the colleges and institutions in the United States which are members of the National Council for Textile Education. But I feel that the title of Mr. Hayward's paper gives promise of more complete coverage than he has in fact provided for your readers.

I believe that any survey of textile education in the United States should indicate the educational role of the Textile Division of the Massachusetts Institute of Technology. At the risk of appearing biased toward the Institute with which I am associated, I should like to venture a few words to indicate the nature of the Institute's textile activities.

Textile education was formally initiated at M. I. T. in 1872. In the ensuing 30-year period well over

1000 students studied fabric design in this special Institute program. In 1903 this design course was transferred to the Boston Museum of Fine Arts.

Starting in 1883 mechanical engineering students at M. I. T. were given courses in the design of textile machinery and of textile mills. Since that time, numerous textile enterprises have been under the guidance of men in many executive capacities who originally obtained their first ideas of textile manufacturing, mill construction, and machine design from these early courses at M. I. T.

In 1885 a textile engineering option was included in M. I. T.'s course in Mechanical Engineering, leading to an S. B. degree. This option has been modified to give increased emphasis to modern concepts of textile technology and has continued to the present day. Numerous students in other Institute departments have taken courses given in this option, thus broadening their backgrounds in chemical engineering, industrial engineering, chemistry, economics, and even architecture.

In 1927 there was a demand for additional work adapted to the needs of men transferring from textile schools, as well as for M. I. T. students. Accordingly, courses in textile technical analysis, microscopy, textile research methods, and statistics were introduced at the graduate level by Professor E. R. Schwarz, present head of the Textile Division. These courses formed the basis for the S. M. degree in Textile Technology, of which 57 have been granted to date. The majority of these men hold responsible positions in the world of textile research, and many are well known as pioneering contributors to this Journal. In this connection it is interesting to note, for example, that last year M. I. T. men held key positions in nearly every national professional textile society.

By World War II the Institute's educational program was broadened to provide for the award of the Sc. D. degree, granted for study and research in the textile sciences. The Textile Division makes no attempt to teach more than a fraction of the material required for this Sc. D. degree. Instead the graduate textile student is expected to develop a background in science, engineering, or industrial management through course work in any of the 20 M. I. T. departments, ranging from Aeronautical Engineering to Physics.

The formal textile courses given at M. I. T. utilize the students' background in classical subjects and emphasize the most recent applications of engineering and scientific fundamentals to textile technology. The textile material taught includes textile technical analysis, textile microscopy, basic fabric structure, experimental planning and analysis, and principles of textile manufacturing. More recently emphasis is being placed on the applied mechanics of textile structures, on the rheology of fibrous materials, and on the dynamics and mechanisms of textile processing. These three important phases of textile technology are receiving corresponding emphasis in graduate student and senior staff researches. However, the doctoral candidate may select any research problem pertinent to the textile industry with either physical or chemical emphasis.

Historic location of the Textile Division in the Mechanical Engineering Department has understandably led to heavy emphasis being placed on the mechanical side of textile technology. This emphasis has led to closer association between activities of the Textile Division and those of the more general fields of Applied Mechanics, Machine Design, Heat Engineering, and Materials. The combination of these fields at the graduate engineering level is unique in this country. Judging from the progress made in other countries in the field of processing dynamics, this M. I. T. program warrants the understanding and encouragement of the textile industry.

The Textile Division has further extended its educational influence through the medium of summer courses and special research symposia. The first of many such special sessions was held in 1929, and continued industry interest has justified frequent revisions and presentations of the program material. The last three programs, on textile structural mechanics, stress-strain behavior, and parachute technology, drew over 300 industry and government representatives from the United States and foreign countries.

I feel that the educational and research activities cited above complement rather than compete with the programs of the textile schools and institutions referred to by Mr. Hayward. The listing of such activities should therefore aid in rounding out your readers' view of textile education in the United States.

STANLEY BACKER
Associate Professor of Mechanical Engineering

INDUSTRIAL SECTION

Measurement of the Needle Heat Generated during the Sewing of Wool and Wool-Nylon Fabrics

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Abstract

A procedure for measuring the temperatures reached by sewing-machine needles during high-speed sewing is presented along with a quantitative evaluation of the effectiveness of several sewing finishes in reducing needle heat. It is shown that the use of sewing finishes on fabrics made of blends of nylon and wool can effectively reduce needle temperatures substantially below the melting point of nylon and thus prevent needle encrustation during production sewing of these fabrics.

I. Introduction

The problem of excessive needle heat in the sewing operation has always been present, but with the advent of synthetic fabrics and threads and faster machine speeds it has become more critical. Synthetic fabrics and synthetic blends are subjected to temperatures above their softening points and a melt or encrustation often adheres to the needle, filling the groove and eye and causing thread breakage. In heavy cotton and all-wool fabrics, the needle heat often damages the sewing thread, leaving weakened seams if actual breakage does not occur.

This problem can be alleviated by special fabric finishes that reduce friction and, consequently, the heat generated by making the fabric yarns and fibers more slippery to the needle.

In some fabrics the problem is handled by reducing machine speed, or by more intermittent operation. This is hardly a satisfactory solution.

Some success has been achieved through the use of needle coolers. Compressed air, water sprays, and wetting or oiling the thread have been tried. No one method has been a complete success or is entirely satisfactory from the standpoint of acceptability by the machine operator and manufacturer.

The objective of this report is to indicate a suitable method of measuring needle heat and to show some preliminary data on the magnitude and distribution of the heat generated by needle friction. Study is also made of the effect of two fabric finishes and the effect of blending a small percentage of nylon with wool in changing the frictional characteristics of wool serge fabrics.

2. Materials and Apparatus

a. Fabric

Cloth, wool, serge, 16 oz, O.D. 33, and cloth, 85% wool–15% nylon, 16 oz, O.D. 33, were used, each tested untreated and treated with two finishes, identified as Finish A and Finish B, as follows:

1. All-Wool: Untreated
   Finish A
   Finish B
2. Wool-Nylon (85–15): Untreated
   Finish A
   Finish B

b. Machine

Union Special 51500 LZ. (Ordinarily this heavy-duty machine would not be used for sewing wool fabrics, but it was felt that preliminary qualitative

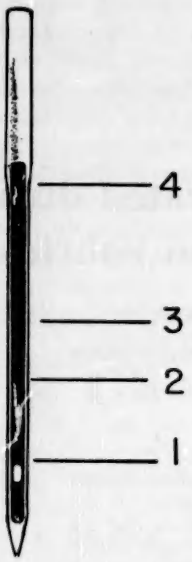

Fig. 1. Position of thermocouple junctions on the needle.

results would be obtained more easily with this apparatus.)

c. Needles

Union Special Needles, Type 143G, Size 080, round shank, round point, double groove, chromium-plated, were used.

d. Thermocouples

Lengths of 30-gauge constantan wire were silver-soldered in the back groove in each of several needles at various positions. An Alnor portable pyrometer with temperature compensator was used to detect the generated potential during the sewing operation.

3. Procedure

Samples consisted of 4 layers of fabric about 8 in. wide by 2 yd long joined at the ends to form a belt which could be stitched continuously around the bed of the sewing machine. The constantan wire from the needle junction was connected to the positive terminal. No needle-cooling apparatus was used in these tests. The sewing machine was run at 3200 rpm, without thread (the thermocouple wire prevented the use of thread) until an equilibrium temperature was noted, usually in about 10 sec.

It was noted that needle temperatures rose immediately after stopping the machine. These increases were recorded, along with visual observations on the reaction of the fabric to the heat generated.

The points at which the constantan wires were soldered to the needles are shown in Figure 1. The junction of the wire and the needle formed a thermocouple which was calibrated in an electric furnace for increasing and decreasing temperatures. This calibration curve is the same for each junction and is shown in Figure 2.

4. Measurement of Needle Heat

a. Distribution of Needle Heat

In beginning the study of needle heat it was thought desirable to determine the hottest region of the needle and to attempt to correlate this temperature with that of the needle butt (position 4, Figure 1). If a good correlation existed, the wire could be soldered to the needle butt where it would not affect needle-fiber friction, and sewing thread could be used in the needle during the sewing operation. Actually, if thread were used in the needle, the temperatures would be from 10 to 30° cooler, depending on the thread used.

Table I shows the distribution of needle temperature at the 4 points along the needle for the 6 fabrics tested. The temperature values in position 4 were considered too low to give accurate extrapolation to other needle regions, despite a fairly good ranking, because the surface deposits affected the resultant temperatures. The hottest region (position 3) was found to be close to the point of deepest penetration of the needle into the fabric.

It would be impossible to solder a wire to the

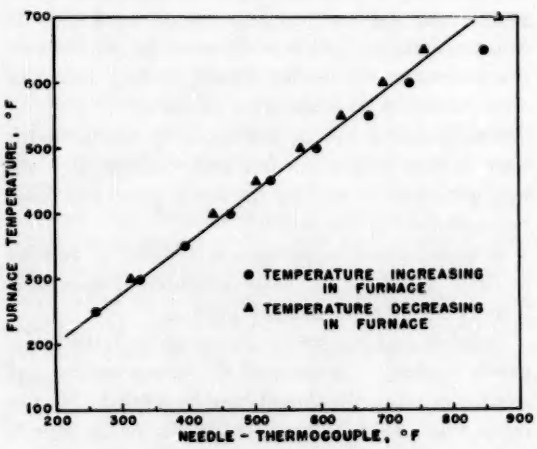

Fig. 2. Calibration of constantan-needle junction of portable pyrometer.

TABLE I. Equilibrium Temperature Reached in Continuous Sewing * (in °F)

Fabric	Thermocouple Junction Position 1	2	3	4	Observations
Wool					
Untreated	545	535	585	170	Strong odor, char, fiber fuzz, needle holes fused.
Finish A	465	450	520	150	Odor, needle holes fused.
Finish B	375	405	424	132	Slight odor, needle holes slightly fused.
Wool-Nylon					
Untreated	440	442	505	155	Strong odor, encrustation, melt, needle holes fused.
Finish A	395	412	455	145	Slight odor, slight encrustation, needle holes fused.
Finish B	380	348	435	120	Little encrustation, slight fusing of needle holes.

* Fabric: 16-oz serge, O.D. 33, 4 layers.
Machine: Union Special 51500 LZ.
Needle Size: 080 Type 143G, 3200 rpm.

needle point and not have it affect the heat generated by its own bulk. At any other needle position, the wire fits into the needle groove with a minimum of protrusion. Actually, the comparison of temperature above and below the needle eye was approximately obtained by running tests on cotton duck fabrics without thermocouples. The needles were examined for discoloration due to heat, and it was found that it was possible to get heat discoloration of the needle region between positions 1 and 3 without affecting the needle surface below the eye.[1] This can be seen in Figure 3.

b. Effect of Fabric

It can be seen from the table that untreated all-wool fabric generates the highest degree of needle heat. This is to be expected because of the nature of the wool-fiber surface. The heat generated is the result of needle and fiber friction and is related to

[1] These results would apply only to this particular type of needle. Experiments have been made by other laboratories with reducing needle heat by using narrow-shank needles, which would necessarily place the highest temperatures nearer the needle eye.

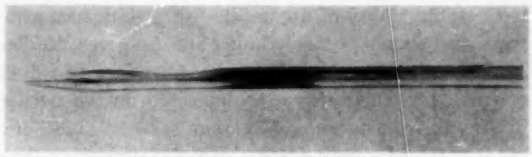

Fig. 3. Heat discoloration of sewing needle.

surface characteristics of the fiber material and to density or tightness of the fabric, as well as to machine speed. Wool is better able to withstand this higher heat; consequently, fabric and needle damage was not a great problem until the advent of higher machine speeds and synthetic materials.

c. Effect of Stopping Machine

Figure 4 shows the data in Table I in bar-graph form and in addition shows the instantaneous rise in temperature when sewing is stopped. This temperature rise might not affect the fabric very much, since part of the time the needle would not be touching the fabric or would be touching only a small surface area. However, the sewing thread in the groove and eye of the needle is generally held against the surface with considerable tension. Most of the temperatures rose considerably higher than the softening point of all thermoplastic synthetic sewing thread and high enough to cause some degradation in most cotton threads.

It will be seen that the untreated all-wool fabric produced the largest increase in temperature when sewing was stopped. This temperature rise is re-

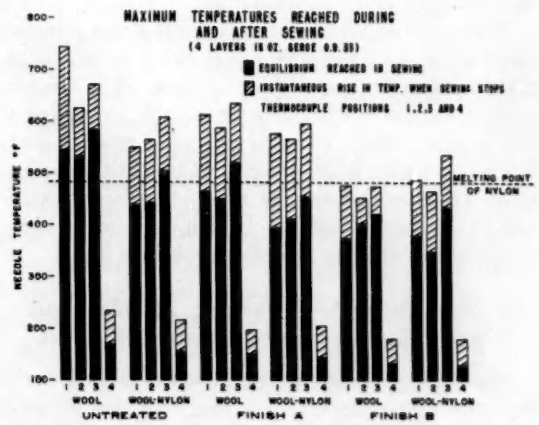

Fig. 4. Maximum temperatures reached during and after sewing (4 layers of 16-oz serge, O.D. 33).

lated to the ability of the needle to transmit heat outward and should be fairly uniform for a given needle. However, it was noted that a dry fiber fuzz and dust of small broken fibers were deposited on the needle by the all-wool fabric. This was easily cleaned off, but it acted as a temporary coating of insulation that raised surface temperatures considerably by retarding heat dissipation.

It is difficult to explain why the increase in temperature for the wool-nylon fabric treated with Finish A should be higher at each junction position than the corresponding increase for untreated wool-nylon fabric. It is possible that, although chemical finishes reduce needle temperatures, they can reduce heat dissipation, thus causing higher internal needle temperatures.

In any case the internal needle temperature must be considerably higher than that measured on the surface. Actually, the needle is air-cooled during the sewing operation. Moving at 3200 rpm with a 1¼ in. stroke corresponds to an intermittent vertical air stream against a stationary needle with an average speed of 1000 ft/min. It is this air cooling that keeps needle-surface temperatures above and below the fabric lower than those in frictional contact with the fabric.

Consequently the heat flow inward is great enough to build up the interior needle temperature above the average surface temperature. Upon stopping the machine the cycle is reversed, the heat flowing back to the outer surface from the needle center. The rise in surface temperature will be dependent upon the amount of heat stored, the temperature, and the heat-flow barriers on the needle surface.

It was noted that the temperature rise was greatest when the surface was coated with either broken wool fibers or a nylon encrustation or melt. The cleaner surfaces of the needle were better able to dissipate this internal heat. For this reason, it was felt that the needle region below the eye, which remained relatively clean and where the ratio of surface area to mass is higher, would not be subjected to as high temperatures as those recorded in position 3.

5. Heat Generated in Sewing All-Wool and Wool-Nylon Blends and Effects of Finishes

The heat generated by the blended fabrics, both untreated and treated, is less than that for the corresponding wool fabrics. The nylon-fiber surface is more slippery to the needle than the scale-like wool-fiber surface.[2] However, nylon has a melting point of about 482°F, and it forms melt and fused needle holes in the fabric at lower temperatures than those that can cause difficulty with the all-wool fabrics.

The effect of fabric finishes can be seen either from Table I or Figure 4. The melting point of nylon was exceeded by the equilibrium temperature of the needle at position 3 for the untreated wool-nylon serge. This would necessarily cause melting and encrustation on the needles, making continuous sewing impossible. Both finishes reduced the equilibrium temperature to a point below the critical temperature.

In actual production, finishing has eliminated much of the initial problem of excessive heat in nylon blends, but little has been done to classify or evaluate finishing treatments as to effectiveness. According to this test, Finish B is more efficient in lowering needle temperatures. However, although both finishes were applied so as to make up approximately 5.1% of the finished fabric weight, Finish A is known to contain more volatile matter. Consequently, the slightly better cooling action of Finish B may be only a result of higher finish concentration.

In any event, the measurement of needle heat provides a method of evaluating finishes and determining optimum finish concentration for improved fabric sewability.

6. Conclusions

a. The heat generated by frictional contact of needle and fabrics is principally a function of fiber surface frictional characteristics and of fabric tightness. Less heat is generated by blended fabrics than by all-wool ones because the coefficient of friction of the synthetic material is lower.

b. Although less heat is generated by the blended fabrics, most synthetics have lower softening points and less inherent insulation due to physical structure; consequently, the problem of fabric damage and thread breakage is more serious.

c. The interior of the needle is at a higher temperature than the surface after equilibrium temperatures are reached in sewing. Consequently, the highest temperatures are reached just after the stopping of the sewing operation when the needle is no longer air-cooled by its own motion.

d. Finishing treatments reduce needle heat by reducing friction, making the fibers more slippery to

[2] The same condition applies to most other blends of synthetics with wool.

the needle. There are insufficient data on the effectiveness and optimum concentration of finishes used to improve sewability and on their effect on internal needle temperatures.

7. Recommendations

The data presented in this report suggest that some specific changes in needle design should reduce needle temperatures. The following examples are given:

a. The holes should be punched in the needle shank above the eye to increase surface area-to-mass ratio and decrease heat stored by the needle. This would also make cooling during sewing more efficient and make cooling by compressed air more effective.

b. The needle shank should be grooved to increase the area exposed to normal air cooling due to machine operation or compressed air cooling and to increase heat dissipation due to radiation.

c. Provision should be made for partial internal cooling through the needle butt by compressed air or gas, since needle internal temperatures are higher than surface temperatures during and just after the sewing operation.

8. Acknowledgments

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Chemical Properties of Field-Weathered Cotton

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This paper deals with the chemical changes in cotton fiber through field weathering. The chemical changes which occur are important for several reasons. Structural changes in the cellulose molecule which have an effect on dyeing occur. Cellulose chain length is decreased [3] and ultimately the utility of the cotton suffers. Previous work [6] on the physical properties of weathered cotton gave indications of length shrinkage which may be interpreted as possible structural changes in the cellulose molecule (crystallinity).

Marsh and coworkers [9] have published extensively on cotton-weathering research. In the publication cited, they have also reviewed the literature.

Work undertaken here attempts to evaluate weathered cotton through chemical tests. The early cotton was field weathered up to 5 mo, whereas the later cotton was in the field for more than 2 mo. Since cotton varies in composition from early to late opening, an additional weathering variability has been added to cotton-weathering research.

[1] Fiber and Spinning Laboratory of the Cotton Research Committee of Texas.

Experimental

The field plans of the experiment were given in a previous publication [6] and will not be repeated here.

Degree of polymerization determinations were made by forming cellulose nitrate and dissolving the nitrate in butyl acetate. The intrinsic viscosity was calculated from the equation of Baker as modified by Philippoff [11] in which $[\eta] = 8/c\ (\eta r^{1/8}-1)$. A correction in intrinsic viscosity was made for incomplete nitration by the method suggested by Lindsley [8]. Degree of polymerization was derived from the Staudinger expression $DP = K[\eta]$ where $K = 118$ for cellulose nitrate in butyl acetate. The value of K was chosen after the review of the literature. This constant affected the magnitude of the DP value but plays only a small part in weathered difference in DP calculations.

Copper reduction values and aqueous-extract pH were run according to the methods outlined by Marsh [9].

Carboxyl groups were determined by the method of Pacsu [7], in which an excess of dilute NaOH is

added to the sample, followed by a back-titration with dilute sulfuric acid in the presence of phenolphthalein.

From the copper reduction values, a carbonyl group equivalent was determined.

Dye-absorption tests were made with Coprantine Green G (Ciba). Dye absorption was determined by measuring the dye concentration before and after dyeing with the aid of spectrophotometry. Dye-molecule aggregation was at a minimum with the dye used.

Cellulose was determined by boiling the sample in 25% monoethanolamine in ethylene glycol [2].

Crystallinity measurements on cellulose were by absorption of iodine [4].

Results

Chemical changes in cotton fiber caused by field weathering were determined. Perhaps the most revealing of these tests was the determination of cellulose viscosity, which measures change in degree of polymerization of the cellulose molecule. Tables I and II give the results of these tests on cotton fiber which was extensively weathered under what might be termed dry conditions. The cellulose nitrate viscosity method detects degradation of two kinds brought about largely through moisture, sunlight, and temperature change. If the cellulose nitrate viscosity is run on cotton before and after weathering, a measure of cellulose chain rupture is obtained. Table I shows a progressive decrease in cellulose *DP* from no weathering through the 149 days of the experiment. Table II gives the percentage change in *DP* through the weathering period for cotton opened on September 4 and November 9. The earlier-opened cotton had a decrease in *DP* of 16.4% due to weathering for the 149-day period, whereas the cotton which opened later had a decrease of 9.0% for the 67-day period. That weathering was more intense in the earlier-opened cotton may be shown by determining the *DP* change for 67 days for the cotton which opened September 4. A value of 14.3% was obtained for September 4, as compared to 9.0% obtained for November 9. When the weathered cotton was alkali-boiled, another *DP* value was obtained, which was due to breaking oxygen bonds from weathering oxidation. A *DP* decrease

TABLE II. The Effect of Field Weathering on Cotton Cellulose Degree of Polymerization

Type of Degradation	Cotton Opening Date 9–4 Change in *DP* (%)	Cotton Opening Date 11–9 Change in *DP* (%)
1. Cellulose chain rupture (Raw cotton *DP* over weathering period)	−16.4	− 9.0
2. Initial cellulose oxidation (Raw cotton *DP*—alkali-boiled *DP*, no weathering)	−13.8	− 9.2
3. Average oxidation (Raw cotton *DP*—alkali-boiled *DP*, from averages)	−13.5	− 9.3
4. Weathering oxidation (Alkali-boiled cotton *DP* difference, over weathering period)	−15.4	−10.9
5. Total degradation (*DP* unweathered cotton—*DP* alkali-boiled cotton, over weathering period)	−27.0	−18.9

TABLE I. Cellulose Degree of Polymerization of Field-Weathered Cotton and Unweathered Cotton

Date Opened	Days in Field	Raw Cotton *DP*	Alkali-Boiled* Cotton *DP*
9–4	0	8402	7241
9–4	11	8262	7082
9–4	24	8284	6938
9–4	38	8213	6803
9–4	52	7620	6732
9–4	66	7203	6236
9–4	84	7564	6514
9–4	98	7649	6832
9–4	115	7410	6436
9–4	133	7275	6455
9–4	149	7023	6129
	Av.	7719	6672

Date Opened	Days in Field	Raw Cotton *DP*	Alkali-Boiled* Cotton *DP*
11–9	0	8576	7787
11–9	18	7998	7285
11–9	32	7835	7174
11–9	49	7805	7134
11–9	67	7803	6948
	Av.	8003	7265
9–4	0	8402	7241
9–15	0	8327	7816
9–28	0	8331	7912
10–12	0	8251	7469
10–26	0	8475	7768
11–9	0	8576	7787
	Av.	8393	7666

* 1 hr boil in 1% NaOH.

TABLE III. Cellulose Content of Field-Weathered Cotton and Unweathered Cotton

Opening Date	Days in Field	Cellulose (%)	Opening Date	Days in Field	Cellulose (%)
9–4	0	93.0	11–9	0	95.0
9–4	11	95.2	11–9	18	94.3
9–4	24	95.0	11–9	32	94.3
9–4	38	95.6	11–9	49	94.7
9–4	52	94.9	11–9	67	94.8
9–4	66	94.9			
9–4	84	95.8		Av.	94.6
9–4	98	95.3			
9–4	115	95.3	9–4	0	93.0
9–4	133	96.8	9–15	0	95.8
9–4	149	95.6	9–28	0	94.1
			10–12	0	95.3
	Av.	95.3	10–26	0	94.5
			11–9	0	95.0
				Av.	94.6

of 15.4% is shown in Table II for this type of cellulose degradation for the early opened cotton. The combined degradation from cellulose chain rupture and cellulose oxidation was a 27.0% decrease in *DP* for the 149-day weathering period. For the cotton which opened on November 9 the degradation from cellulose oxidation was 10.9%, and the combined degradation from weathering over a 67-day period was 18.9%. From the viscosity determination on raw cotton and alkali-boiled cotton, it is apparent that oxidation takes place as soon as the cotton opens. This initial oxidation shows a decrease in *DP* of 13.8% for the early cotton, as compared to 9.2% for the late cotton. The data show the effect of the season on cellulose oxidation.

Table I also shows the *DP* of raw and alkali-boiled cotton which opened at approximately 2-wk intervals over a 2-mo period and was harvested without weathering. The cellulose *DP* values were quite consistent over the 2-mo period with a slight increase in the late-opening cotton. The cellulose degradation through weathering was slightly more than 8.0% for the average for these samples.

TABLE IV. Aqueous-Extract *p*H of Field-Weathered Cotton and Unweathered Cotton

Opening Date	Days in Field	Raw Cotton (*p*H)	Opening Date	Days in Field	Raw Cotton (*p*H)
9–4	0	7.04	11–9	0	6.22
9–4	11	6.41	11–9	18	6.47
9–4	24	6.33	11–9	32	6.44
9–4	38	6.80	11–9	49	6.10
9–4	52	6.81	11–9	67	6.00
9–4	66	7.27			
9–4	84	6.75		Av.	6.22
9–4	98	6.51			
9–4	115	7.14	9–4	0	7.04
9–4	133	6.99	9–15	0	6.88
9–4	149	7.10	9–28	0	6.38
			10–12	0	6.21
	Av.	6.83	10–26	0	6.32
			11–9	0	6.22
				Av.	6.51

The main reason for running cellulose was to detect gain of cellulose with time in the field. However, the cellulose content of the samples in Table III was not too revealing. There was a rather consistent cellulose content in most of the samples. The late-opening weathered cotton averaged 94.6% of cellulose. The cotton with no weathering which opened September 4 had a cellulose content of 93.0%, whereas the average of these weathered samples was 95.3% and the average of the last five samples was 95.8%, or 2.8% more cellulose than the samples with no weathering. This would indicate a loss of extraneous material other than cellulose through field weathering.

The *p*H of the aqueous extract of weathered cotton shows whether biological decay has taken place in the cotton through microorganisms. The *p*H data are shown in Table IV. A rise in *p*H over the value obtained for the nonweathered cotton indicates whether biological decay occurred. In the cotton which opened on September 4 and weathered in the field for 149 days, the *p*H remained fairly constant, indicating no biological decay. The samples which opened November 9 had an even lower *p*H than that of the cotton opened on September 4. The November 9 cotton showed an insignificant decrease in *p*H with time in the field. Samples of cotton which opened from September 4 until November 9 at intervals of approximately 2 wk showed a decrease of *p*H from 7.04 to 6.22, indicating cotton which opened late in the season was of a more acidic nature or higher in constituents such as organic acids.

Copper reduction values of weathered cotton are shown in Table V. A value of approximately 1.0 for the early opening cotton with no weathering to 0.08 for the cotton in the field for 149 days shows that the reducing compounds of weathered cotton were perhaps oxidized to nonreducing substances in a period of about 53 days of field weathering, even under dry conditions. The weathered samples which opened late in the season had a substantially lower initial copper reduction value and were not as subject to oxidation as the earlier-opened cotton. Lower light intensity and lower temperatures may have slowed down the oxidation of copper-reducing sub-

TABLE V. Copper Reduction Value of Field-Weathered Cotton and Unweathered Cotton

Date Opened	Days in Field	Copper Reduction Value	Date Opened	Days in Field	Copper Reduction Value
9–4	0	0.98	11–9	0	0.58
9–4	11	0.61	11–9	18	0.57
9–4	24	0.86	11–9	32	0.52
9–4	38	0.41	11–9	49	0.40
9–4	52	0.12	11–9	67	0.38
9–4	66	0.18			
9–4	84	0.22	9–4	0	0.98
9–4	98	0.14	9–15	0	0.93
9–4	115	0.17	9–28	0	0.79
9–4	133	0.13	10–12	0	0.81
9–4	149	0.08	10–27	0	0.83
			11–9	9	0.58

stances. In the samples with successive opening dates, there were indications of less reducing materials as the opening date advanced through the harvest season.

Table VI shows the effect of field weathering on dyeing of cotton fiber. Oxidation of carbonyl groups and increase in carboxyl group are believed to influence the decreased absorption of direct dyes by weathered cotton. Crystallinity as a measure of internal surface area was not changed through weathering and therefore was not considered as a contributing factor in decreased dye absorption.

Discussion

Physical changes in field-weathered cotton fiber are hard to detect. The physical tests on these samples [6] showed length decrease and color increase. Fineness, strength at zero gauge, and maturity showed no appreciable differences. Marsh [9] was able to show strength differences due to weathering using $\frac{1}{8}$-in. gauge breaking distance and a slight length decrease. A decrease in elongation in this same work is of interest, since it indicates structural change in the fiber or alteration in chemical composition brought about by sloughing of materials other than cellulose. Cellulose values in Table III show an increase in cellulose with time in the field which could only take place by a loss of extraneous materials other than cellulose. Structural changes as measured by crystallinity have not been materially affected by field weathering (Table VI). Cellulose degree of polymerization shows chain rupture and oxidation which could eventually affect tensile strength and fiber elongation. Conrad [1] has shown a close relationship between cellulose chain links broken and fiber strength lost and also that elongation increases with the percentage of links broken.

The chemical tests reported herein were selected to give as much information as possible on field-weathered cotton. An aqueous-extract *p*H on raw cotton indicates biological decay is at a minimum. Therefore, chemical tests are largely centered on field damage due to temperature and light intensity. Thus, the weathering in this experiment largely caused a chemical change in the fiber through loss of materials of low molecular weight such as sugar, organic acids, and mineral constituents. Large compounds such as pectic substances, hemicelluloses, pentosans, proteins, and waxes were reduced in size through oxidation and hydrolysis. These large molecules were degraded through weathering and sloughing off, as shown by the increase in cellulose percentage (Table III). Other changes from field weathering were those to the cellulose molecules, such as cellulose chain rupture and oxidation (Table I).

The copper reduction value shown in Table V is largely a measure of free aldehyde groups. Admittedly, this is a rough determination, and other reducing groups enter into the copper reduction value besides cellulose aldehyde groups in a complex organic structure such as cotton fiber. The disappearance of reducing substances through microbiological action should be at a minimum because of lack of moisture during the weathering period. The *p*H values reported in Table IV indicate that biological degradation, if present, is small. Therefore, the loss in reducing value for the weathered samples is evidence of cellulose oxidation. The loss of extraneous materials as indicated by increase in cellulose is hardly enough to account for the sudden

TABLE VI. The Effect of Polar Groups and Cellulose Crystallinity on Dyeing of Field-Weathered Cotton

Cotton Opening Date	Days in Field	Cellulose Crystallinity (%)	Carbonyl Groups (meq/g cellulose)	Carboxyl Groups (meq/g cellulose)	Dye in Fiber (%)
9–4	0	86	0.077	0.015	1.10
10–12	0	86	0.063	0.013	1.25
11–9	0	84	0.045	0.014	1.05
9–4	0	86	0.077	0.015	1.10
9–4	84	87	0.014	0.018	1.00
9–4	133	87	0.010	0.019	0.70
11–9	0	84	0.046	0.014	1.05
11–9	32	87	0.041	0.016	1.00
11–9	67	86	0.031	0.020	0.85

loss of reducing value of the samples. The degradation of the cellulose molecule as measured by decrease in degree of polymerization and shown in Table I is additional evidence that oxidation is responsible for changes in cotton reducing power.

A few dye tests were made on extremes of some of the field-weathered cotton, and these values are reported in Table VI in per cent dye in the fiber. Both the late and early opened cotton show a decrease in uptake of dye due to weathering. The sample in the field for 133 days was noticeably of lighter shade than the other dyed samples. Changes in internal surface area or increase in carboxyl group are necessary for lighter shades using direct dyes when other physical properties are alike. Since crystallinity has shown very little change in weathered cotton (Table VI), internal surface area may be ruled out as a contributing factor in lighter dyeing. Apparently, direct dyes are repelled by increase in negative carboxyl groups [10], which are increased by oxidation through field weathering.

Just what part loss of constituents other than cellulose played in lower dye absorption is open to speculation. Since kiering removes much of this extraneous material other than cellulose in commercial practice, the loss of these materials would be expected to increase dye absorption and not be a factor in lighter dyeing.

Degradation due to field weathering is readily detected by a cellulose nitrate viscosity determination before and after alkali boil (Table I). The loss of viscosity on weathered cotton indicates cellulose chain rupture through oxidation. Furthermore oxidation may be detected through an alkali boil and subsequent viscosity determination [3]. Copper alkaline solution methods break the oxygen bonds and as a result measure total degradation of cellulose. Both forms of degradation increase with time in the field, and degradation is considerably less for the later-opened cotton when considered on a per day weathering basis. Obviously, lower light intensity and temperature play a part in lessening field degradation in the late-opening cotton.

In the samples which were picked at regular intervals over a 2-mo period without weathering, the consistent cellulose content does not conform to the physical properties. Late-opening cotton shows less development as measured by physical properties [5] and under-development of cotton usually indicates lower cellulose content.

The length of time cotton remains in the field will vary with different sections of the cotton belt. Cotton which opens normally will be in the field over a considerable period, depending on the number of pickings. If chemical defoliation is used for mechanical harvesting, picking will be speeded up and, consequently, weathering damage will be at a minimum. When frost is used for defoliation, the exposure to weather will be longer. Therefore, the amount of chemical damage due to field weathering is extreme for many localities. Furthermore, environmental factors also must be considered in evaluating field damage.

Conclusions

Cotton was weathered in the field for regular intervals up to 5 mo, starting on September 4. A second group of samples was weathered at regular intervals for over 2 mo, starting on November 9. All weathering was under what may be considered dry conditions. An aqueous-extract *p*H indicated biological decay was nonexistent in any of the weathered samples. This supports the contention that considerable moisture is necessary for microorganisms to decompose cotton fiber in the field.

In field weathering two types of degradation are reported: the one a complete cellulose chain rupture and the other cellulose oxidation. Total degradation was as high as 27% for the early opened cotton in the field for 5 mo and 18.9% for the late-opened cotton in the field over 2 mo.

Cellulose determination indicates a loss of extraneous materials other than cellulose by showing an increase in cellulose content with time of weathering. This was not evident in the late-opened cotton.

A dye study showed reduction of dye absorption with time of weathering. Since decrease carbonyl groups and increase carboxyl groups are correlated with dye absorption, polar groups in the cellulose molecule are therefore believed to account for lighter dyeing of weathered cotton rather than changes in surface phase. No change in crystallinity helps to substantiate these conclusions.

Cotton samples picked over a period of 2 mo show rather consistent chemical properties. Degree of polymerization decrease with alkali boil indicates instantaneous oxidation on these unweathered samples. Cellulose content was fairly consistent, in spite of the fact that wall thickness was lower for the late-opened cotton [5].

An aqueous-extract *p*H decreases from early to late-opening cotton, indicating extraneous substances

of a more acidic nature. Copper reduction values were also lower for the late-opening cotton, which may be attributed to change in materials other than cellulose.

Acknowledgment

Appreciation is expressed to Mr. Levon Ray, agronomist, Texas Agricultural Experiment Station, Lubbock, Texas, for cotton samples.

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Book Reviews

Worsted Drawing and Spinning, Part I. H. Walker. Manchester, England, The Textile Institute, 1954. 239 pages. Price, $3.00.

Reviewed by A. Ward France, Philadelphia Textile Institute, Philadelphia, Pa.

This is an informative book for anyone interested in the Bradford and French worsted systems of spinning wool. The American system is only mentioned in chapter 8, "Drawing Developments," and there is little reference to synthetics. The first chapter is a good resume of worsted spinning and explains drafts, doubling, weight of roving required, and number of operations required and also gives the requirements of a complete layout for the Bradford system. There are some very interesting points brought out here as to why certain drafts are used, depending on the character of the wool. Different layouts are shown for the same yarn and explanations given of why certain layouts are preferable to others. Much research has been done in England on these problems.

The second and third chapters are on gill boxes and explain in detail why certain modifications have been made for better fiber control. Calculations for draft and twist are given with detailed explanations. Winding details and calculations are given for the Spindle gill box. Chapters four and five give the details on the open and cone draw frames with explanations on fiber control and calculations where applicable. Chapters six and seven deal with the French and Continental systems with interesting illustrations of top used and details of machines. These chapters are very helpful to the student and to anyone who comes in contact with actual production on these machines.

Chapter 8, "Drawing Developments," is especially interesting to everyone connected with worsted spinning because it discusses the effect of reducing operations, maintaining continuity of production, increased speed, increasing delivered weights, and the reduction of the number of operators, all to lower cost. Production calculations and considerations and stop motions and faults are covered in the last two chapters. Faults and suggested corrections are well covered and the use of the new Roper Autoleveller is explained in this connection.

In English spinning, quality is first and the question is how can the above be handled and not lower quality. The American system is here mentioned as an experimental system based on modified cotton equipment. While improvements are being made in the machines of the American system, the low number of operations and the single end fed to the roving machine make it hard for this system to compare to either the regular Bradford or the French system for quality of yarn produced, according to the author.

Starch and Its Derivatives. Third Edition (Revised). Volumes I and II. J. A. Radley. New York, John Wiley & Sons, Inc., 1954. xi + 465 pages; xi + 510 pages. Price, $10.00 each volume.

Reviewed by Eugene Pacsu, Princeton University, Princeton, N. J.

Need for a new edition only a short time after the appearance of a book is usually most gratifying to the author for it shows sustained interest in the topic and general appreciation of his endeavor. It also offers him an opportunity for necessary revision and inclusion of up-to-date information on the accumulated knowledge in the ever-expanding field of his subject. The early exhaustion of the first and second edition of Radley's book on *Starch and its Derivatives* (1940, 1943) and the similar fate of the two editions of Kerr's *Chemistry and Industry of Starch* (Academic Press, Inc., 1944, 1950) would indicate a great demand for information on this important natural product, equally attractive to the chemist and the industrialist. Had the present edition appeared some five years earlier than it did and without the alluring designation "revised" printed under the title, the reader would probably not have experienced a feeling of disappointment after acquiring and studying it with expectation. As it appears now, the book contains hardly any knowledge not available in the 1950 edition of Kerr's book, and most of the latest references cited in it do not go beyond the years in the middle forties.

One curious feature of the book is the fact that many of the "new" chapters were contributed by authors whose identical chapters had already been printed, mostly word by word, in Kerr's book. Strangely enough, this holds true for at least one of the chapters written by the American editor himself for his own book. From the readers' viewpoint it is disappointing to find that a "revised" book on starch in 1954 should contain a large portion of material from another book which itself is ripe for an up-to-date revision. It is almost ironical that several of the more serious factual errors discovered in the text, for instance the incorrect equation of periodic acid oxidation on pp. 348–49 of Vol. I and reprinted from pp. 312–13 of Kerr's book, occur in these "new" contributions.

There are found, however, some real values in this book in the form of well-written chapters accounting for important phases of starch chemistry. Among these assets the chapter on starch fractionation by Dr. T. J. Schoch is an outstanding example of both scholarly presentation and informative exposition. Another chapter dealing with the chemical evidence for the structure of starch and written by Drs. L. Hough and J. K. N. Jones should be a "must" reading for anyone who desires useful and authoritative information on the present status of the starch problem and on the modern technique of structural investigation of the various starches. Also, the forty-nine photomicrographs of starch granules contributed by E. Young should give the reader a feeling of aesthetic satisfaction.

Being apparently the only book on starch at present available in the English language, it will have to satisfy the demand of a large group of scientific and technical workers who wish to acquire general but not necessarily up-to-date information on the subject.

Mechanics for Textile Students. W. A. Hanton. Manchester, England, The Textile Institute, 1954. Available through Fairchild Publications, New York. 336 pages. Price 25/-.

Reviewed by Milton Hindle, Professor, Lowell Technological Institute, Lowell, Mass.

A timely treatise, *Mechanics for Textile Students* should be in the library of every student of textile engineering. In fact practicing engineers will find it of value.

The wealth of material presented coupled with the final chapter on experimental methods should so stimulate the mind of the student that he can readily develop ways and means of solving the many problems that he will encounter. The chapter on coil friction is of special interest and is specifically slanted toward textiles. Nowhere has the writer seen the subject treated so thoroughly.

The scope of subject matter covered has made it necessary that definitions and development of formulas be brief. Also, the solutions of many problems which will be encountered in actual practice are given. These, together with practical problems for homework, furnish the student with a thorough understanding of the mechanics of textile machines.

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